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Proton Scattering Analysis for Light Elements in Air Particulate Matter

Florida State Univ, Tallahassee Dept of Physics

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Proton scattering analysis has been developed to provide analyses of elements with atomic numbers ranging from 6 to 20 as a complementary method to X-ray analysis. Samples of air particulate matter from both filter and impaction devices have been analyzed and time sequence and particle size information obtained. In combination with X-ray analysis, total mass may be determined by summation of elemental masses; however, further investigation is needed to compare with the gravimetric method. Like X-ray analysis, it has a broad range, and is rapid, subject to automation, and non-destructive of the prepared sample. Analyses of typical atmospheric samples may be performed in five minutes or less. With further development, the method can readily be advanced from experimental to routine usage.

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PROTON SCATTERING ANALYSIS FOR LIGHT ELEMENTS IN AIR PARTICULATE MATTER

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PREFACE

The intent of this report is to summarize our research on proton scattering as it applies to the analysis of samples of particulate matter found in the atmosphere. The most important details (such as kinematics and angular distributions) are treated in the reprints which form the appendices. While the scattering literature of nuclear physics is vast, only articles of direct relevance to the subject matter of this report are included in the bibliography. Included as appendix B is a reprint which describes the computer code REX which serves as the model for computer code SCAT.

ABSTRACT

Proton scattering analysis has been developed to provide light element analyses as a complementary method to x-ray analysis. Samples of air particulate matter from both filter and impaction devices have been analyzed and time sequence and particle size information obtained. In combination with x-ray analysis, total mass may be determined by summation of elemental masses; however, further investigation is needed to compare with the gravimetric method. Like x-ray analysis, it has a broad range, and is rapid, subject to automation, and non-destructive of the prepared sample. Analyses of typical atmospheric samples may be performed in five minutes or less. With further development, the method can readily be advanced from experimental to routine usage.

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SECTION 1

INTRODUCTION

The scattering of protons by the nuclei of elements has been successfully applied to the quantitative analysis of the light elements. The method is broad-range, rapid, subject to automation and non-destructive of the prepared sample. As such, it furnishes an ideal complement to x-ray analysis especially since the necessary sample requirements are almost identical. Absorption of x-rays by the sample itself places a limit on the lightest elements measurable by detection of x-rays. For samples thicker than about 1 mg/cm^2 (or particle sizes about 10 μm) x-ray absorption corrections become difficult for elements of atomic number Z = 13 (aluminum) and below. A proton scattering system was developed to observe the light elements and overlap the lower range of the x-ray technique.

Proton scattering is essentially a form of nuclear mass spectroscopy which may be carried out in an efficient, broad-range fashion utilizing commercially available silicon surface barrier detectors. Figure 1 pictoralizes the elastic scattering of 16 MeV protons by the ^{12}C and ^{28}Si nuclei for three angles. The energies of the scattered protons are predicted using the laws of conservation of mass-energy and conservation of linear momentum. Our earliest exploratory measurements on a size

fractioned aerosol sample from Tallahassee, Florida is shown in Figure 2. Resolution is sufficient to permit analyses up to and including Z = 17, chlorine. Following this initial success, efforts were directed to the design, construction and test of an efficient system suitable for both filter and impactor aerosol samples. This report details the results obtained on samples from field projects, progress on creating a computer code for evaluation of such data and results of supportive calculations (kinematics) and measurements (angular distributions and excitation functions) needed to fully evaluate and define the limits of the system.

TABLE 1 APPROXIMATE DETECTION LIMITS FOR LIGHT ELEMENT PESA DETERMINATION ON TYPICAL AEROSOL FIELD SAMPLES TAKEN ON NUCLEPORE FILTER EXCEPT FOR CARBON WHICH IS REPORTED FOR POLYSTYRENE BACKED IMPACTOR SAMPLES.

Element	3σ Detection Limit ($\mu g/m^3$)
C	0.2
N	0.2
O	1.4
F and Mg	2.0
Na thru Ca	0.5

Using actual aerosol field samples, typical 3σ detection limits for light elements have been calculated and are shown in Table 1. As will be detailed in this report, these limits allow significant measurements on atmospheric particulate matter with time resolution as short as two hours. Carbon determinations are treated in detail in Section 8. All spectra presented in this report are the raw spectra obtained by multichannel analysis with no background subtraction or other treatment.

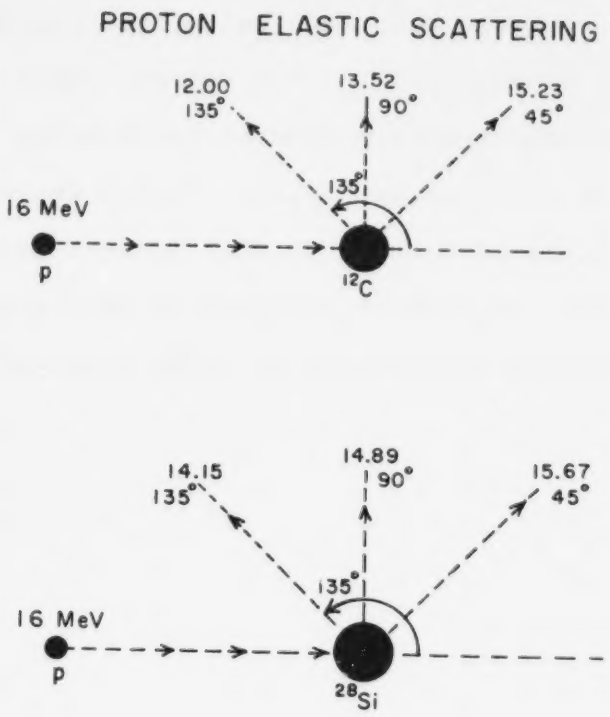


Figure 1. Schematic representation of proton scattering by ^{12}C and ^{28}Si.

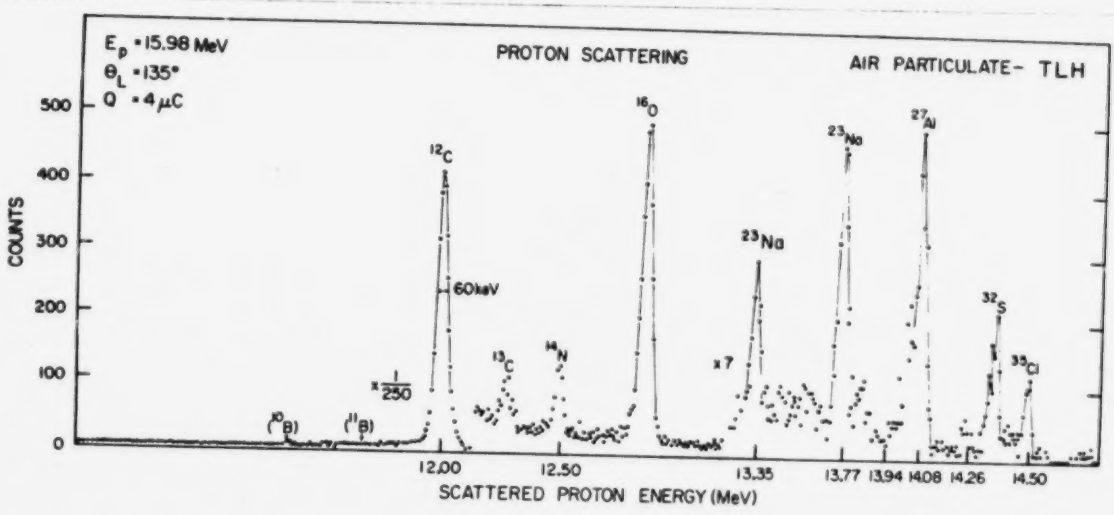


Figure 2. Proton scattering spectrum for an impactor sample.

SECTION 2

CONCLUSIONS

Proton elastic scattering analysis for light elements was developed as the only choice for a broad-range complement to x-ray analysis. Like x-ray analysis it is broad-range, rapid, subject to automation and non-destructive of the prepared sample. Furthermore, it's sample requirements are nearly identical to those of x-ray analysis.

For air particulate matter it has been demonstrated to be effective for both filter and impactor samples to produce both time sequence and particle size information with excellent resolution. In combination with x-ray analysis total mass may be determined by summation of elemental masses. Carbon determinations represent a special problem for any method, in that most of the desirable backing materials contain carbon. This problem appears surmountable by use of thinner filters and impaction surfaces.

SECTION 3

RECOMMENDATIONS

In light of the reported findings proton scattering is recommended for further development in the following aspects:

1. develop more precise determination of carbon content through the use of Teflon filters.
2. explore use of thinner filters to facilitate determination of carbon content of the aerosol while maintaining compatibility with x-ray analysis and excellent time resolution.
3. pursue advanced programming methods for spectral evaluation with emphasis on non-Gaussian peak shapes.
4. move angle of observation from 120 to 135 degrees to enhance sensitivity of other elements relative to carbon.
5. continue to refine the method by application to field samples.
6. add detectors for hydrogen determination.
7. use PESA to better understand the attenuation corrections needed to x-ray analysis.
8. confirm the efficacy of the method for nitrogen determination for aerosol samples.

9. examine and define volatility limits for aerosol samples under analysis conditions.

SECTION 4

PROTON SCATTERING BY PARTICLE DETECTION - THE CHOICE

A variety of nuclear reactions may be used for quantitative measurements of the light elements. Proton scattering was chosen primarily for two reasons. Firstly, its broad-range characteristic enables measurement of all light elements simultaneously in a single bombardment with a single detector. Secondly, proton scattering cross sections are generally higher in value than those of other nuclear reactions. Still another desirable characteristic is the appearance of both the elastic and one or more inelastic peaks in the spectra which provides a definitive "signature" for each element.

Proton inelastic scattering by gamma-ray detection is also a method which was examined. This method has been studied in considerable detail by B. L. Cohen et al[1] with samples of about 200 mg. In order to maximize sensitivity over a range of elements multiple detectors of different sizes should be used depending upon the energy of the emitted gamma ray. Further improvement in sensitivity and selectivity would necessitate bombardments at different energies for different elements on particular substrates. In addition, Germanium detectors for gamma-rays are considerably more expensive than silicon detectors for charged particle observation.

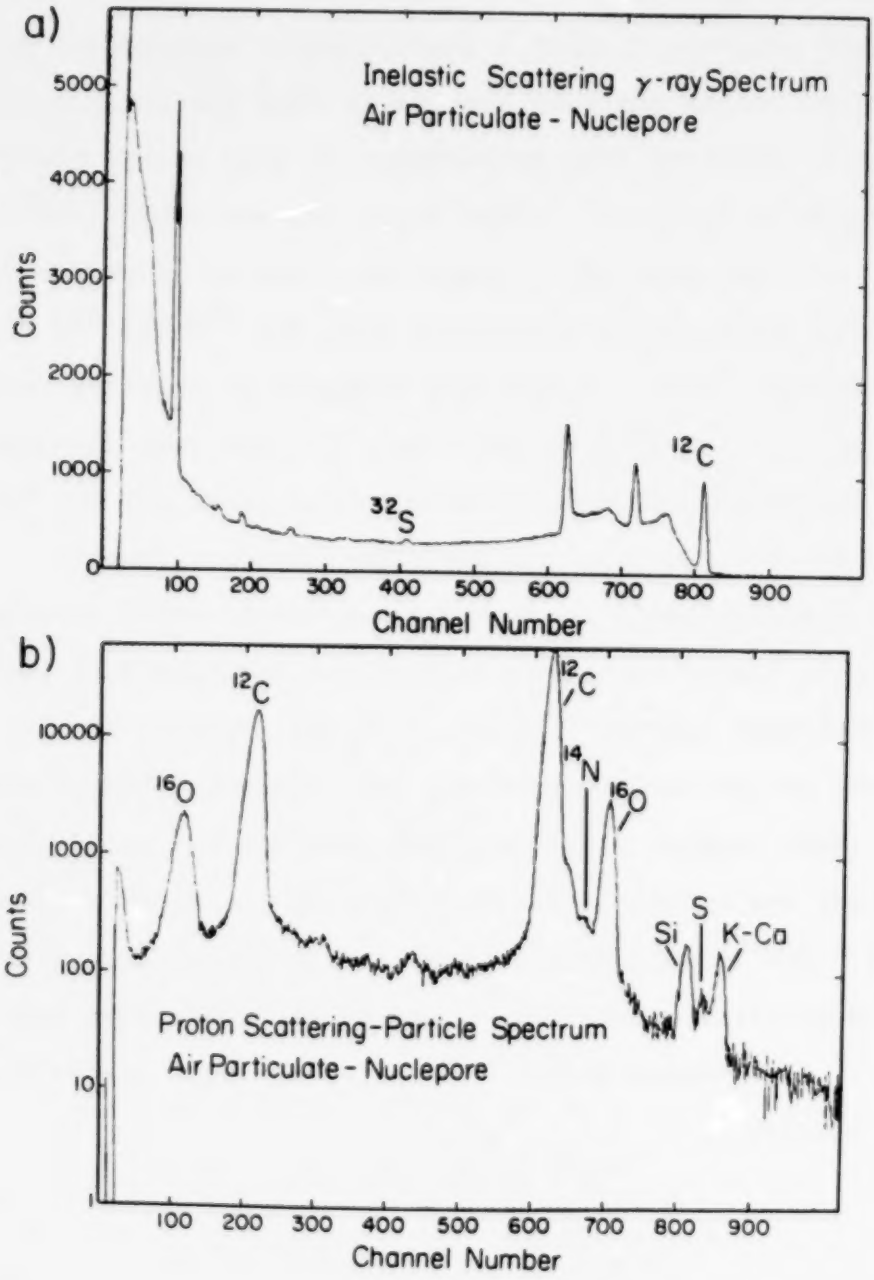


Figure 3 a. Inelastic scattering γ-ray spectrum for a filter aerosol sample.

b. Elastic and inelastic particle spectrum for the same sample and same integrated charge.

Our goal was finding a light element measurement scheme suitable for use on the same samples as used for x-ray analysis. The spectra resulting from bombardment of such an air particulate sample on Nuclepore filter substrate are shown in Figure 3. The inelastic scattering gamma-ray spectrum of Figure 3A reveals the peaks due to scattering from the ^{12}C and ^{32}S first excited states. This spectrum was measured at a proton bombarding energy of 7.0 MeV an 8% efficient, 3.5 keV FWHM lithium drifted Germanium detector. Higher energy peaks due to ^{16}O are excluded due to insufficient bombardment energy, however, if included a considerable increase in background would result. By contrast, Figure 3B shows the particle spectrum from bombardment of the same sample. Carbon, nitrogen, oxygen, silicon, sulfur and potassium-calcium peaks are observed. The potassium-calcium (mass numbers 39-40) are not resolved but could readily be resolved and quantitatively analyzed by the x-ray emission analysis. The above considerations led to the choice of developing the particle scattering method as the most rapid and the only truly broad-range method for analyzing light elements in aerosol samples.

SECTION 5

AIR PARTICULATE ANALYSES

An essential component in the development of a useful analysis tool is the demonstration of the applicability to realistic field samples. Two examples of the application of PESA to typical aerosol samples are given in this section. Figure 4 shows the proton scattering spectrum for an $0.3m^3$ air particulate filter (Nuclepore) sample taken in St. Louis, Missouri. A total of eight elements is observed in a spectrum quite suitable for overlapping with x-ray analysis.

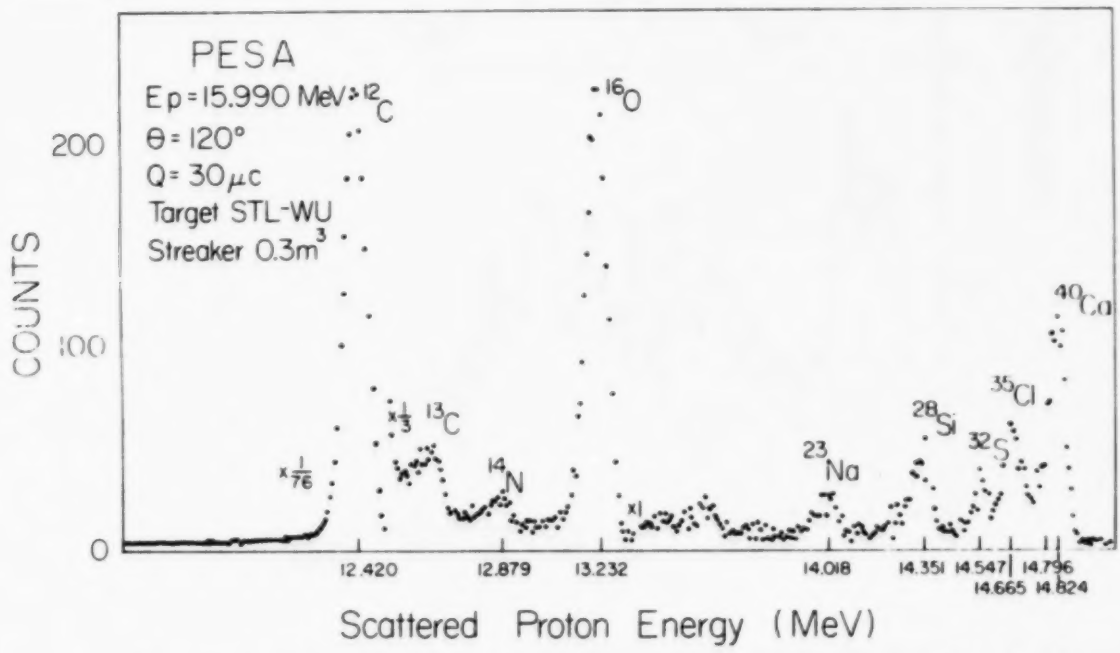


Figure 4. PESA spectrum for an aerosol sample from St. Louis, Missouri.

From similar spectra, the time plots (with two hour resolution) were obtained and are shown in Figure 5,

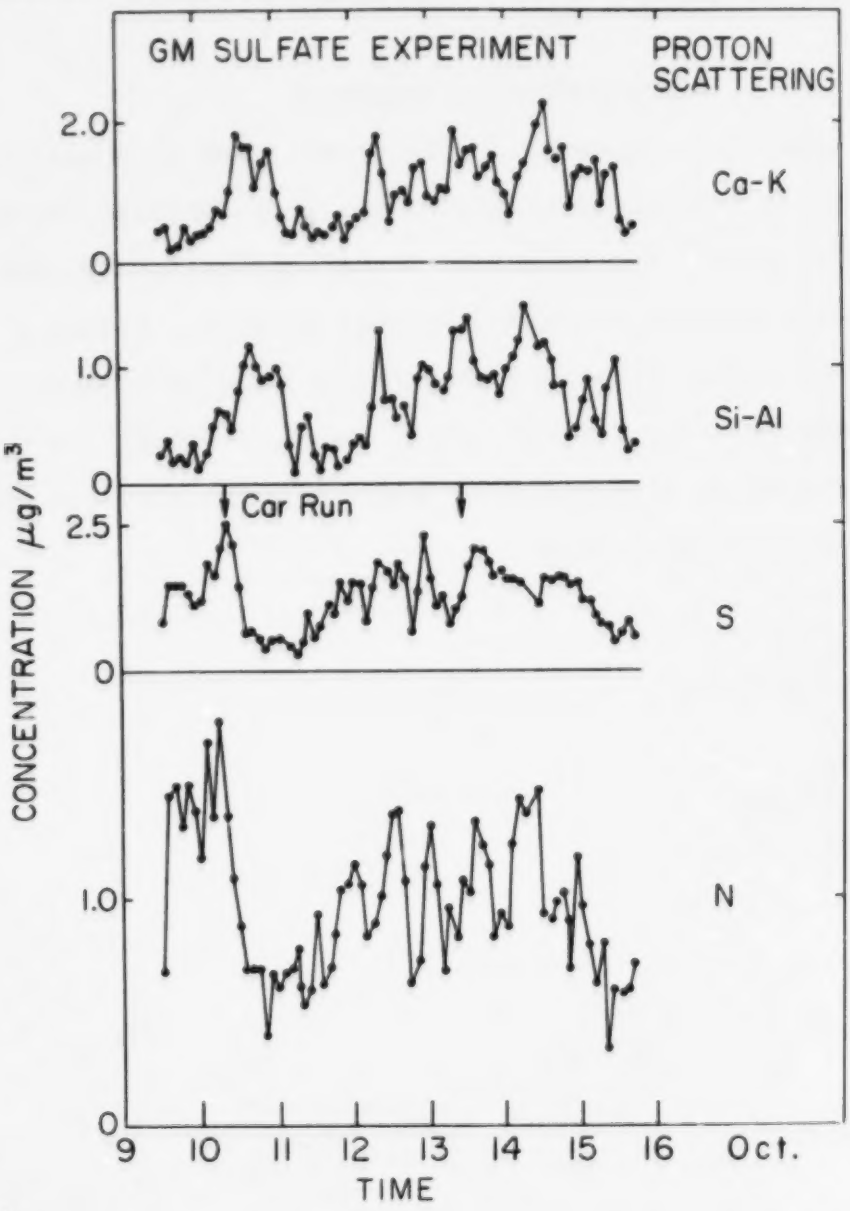


Figure 5. Time plot of PESA data from the General Motors Sulfate Dispersion Experiment.

For particle size analysis, impactor collected particulate matter may be analyzed as shown in Figure 6. Spectra such as these may be used to construct particle size plots as shown in Figure 7.

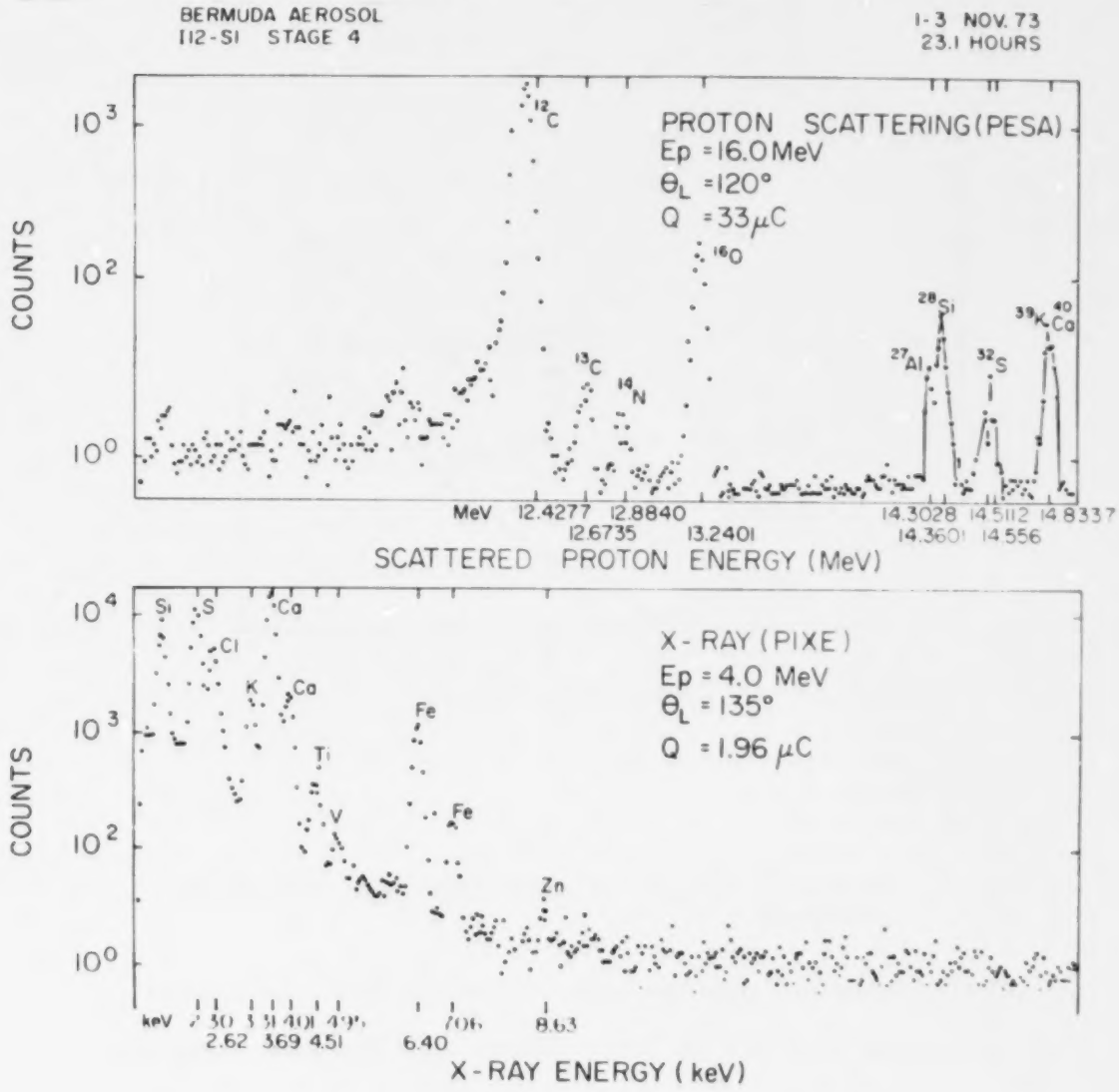


Figure 6. Combined PESA-PIXE analysis of an aerosol sample taken with an impactor.

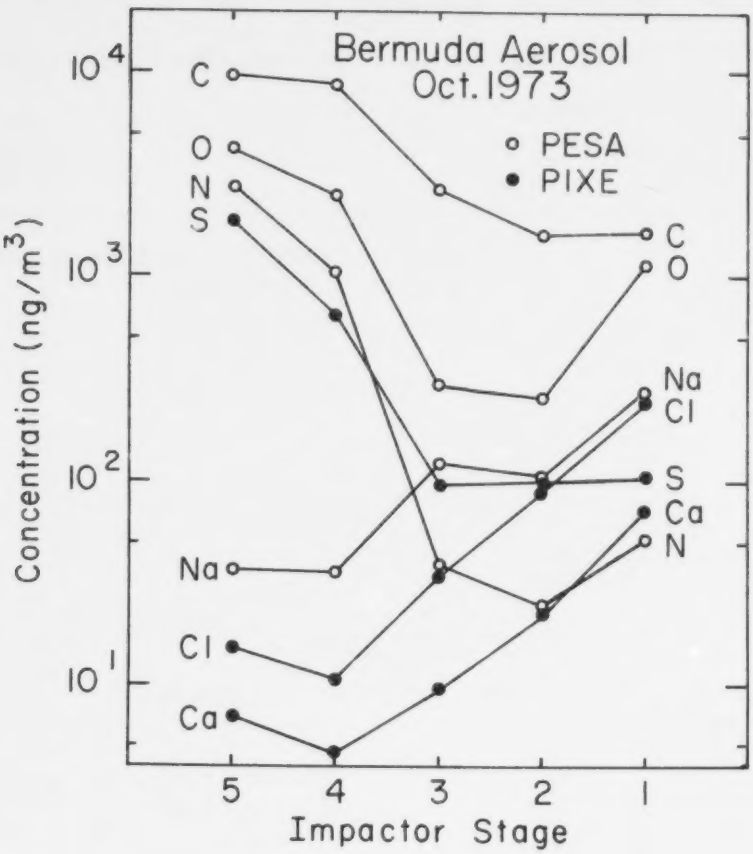


Figure 7. Particle size plot from combined PESA-PIXE analyses.

These examples demonstrate the practical usefulness of PESA technique applied to both filter and impactor samples.

SECTION 6

COMPUTER CODE FOR DATA EVALUATION - SCAT

Central to any rapid, automated spectral analysis method is a peak fitting and data evaluation computer code. The codes SCAT and REX have been simultaneously developed to provide the best possible analyses for PESA and PIXE respectively. Characteristics of the programs are virtually identical with the exception of the shape of the continuum which underlies the peaks. During this grant period more experience has been gained with REX since it was in routine analytic use while SCAT was applied to developmental spectra.

These programs fit spectra containing peaks due to up to 50 elements. Nonlinear least squares Gaussian fits proceed from a library of parameters which describe the spectrum of each element in terms of the peak energies, full widths at half maxima and relative ratios of peak values. For example, the carbon spectrum consists of three peaks while the more complex Al spectrum requires 15 to define it. Following fitting, the areal density (mass/cm^2) is calculated from cross sections determined from standard (usually gravimetric) samples. Since this method is absolute, it need not be completely calibrated for all elements on every unknown determination but only checked with a few standards at the beginning and end of an extended run.

An unusual advantage of this type of program is its use to synthesize spectra and thus determine sensitivity limits for assumed loadings on a particular type of backing. This specific sensitivity determination is the only really meaningful one since it accounts for both the underlying continuum and elemental peak interferences.

Typical standard spectra are shown in Figures 8 and 9. Figure 8 shows peaks due to carbon, nitrogen and oxygen obtained by bombardment of the plastic, Kapton. Figure 9 shows the considerably more complex spectrum due to bombardment of a thin aluminum foil.

Five non-linear parameters allow necessary small shifts in the energy calibration and full width at half maximum necessary when fitting from a predetermined spectral library. An additional ten linear parameters are employed to achieve the fit to the continuum lying beneath the peaks. These parameters were developed by trial and error during the extended period over which the code was being developed. Three or four iterations produce convergence in times of one minute with an overall χ^2 in the range 0.5 to 1.1.

Output of the calculations is available from a line printer or an x - y point plotter. Aerosol concentrations are printed for all elements in the library with 3σ detection limits indicated. In the plot mode the raw data, fitted curve and continuum background curve are all displayed.

User input to operate the program is kept as simple

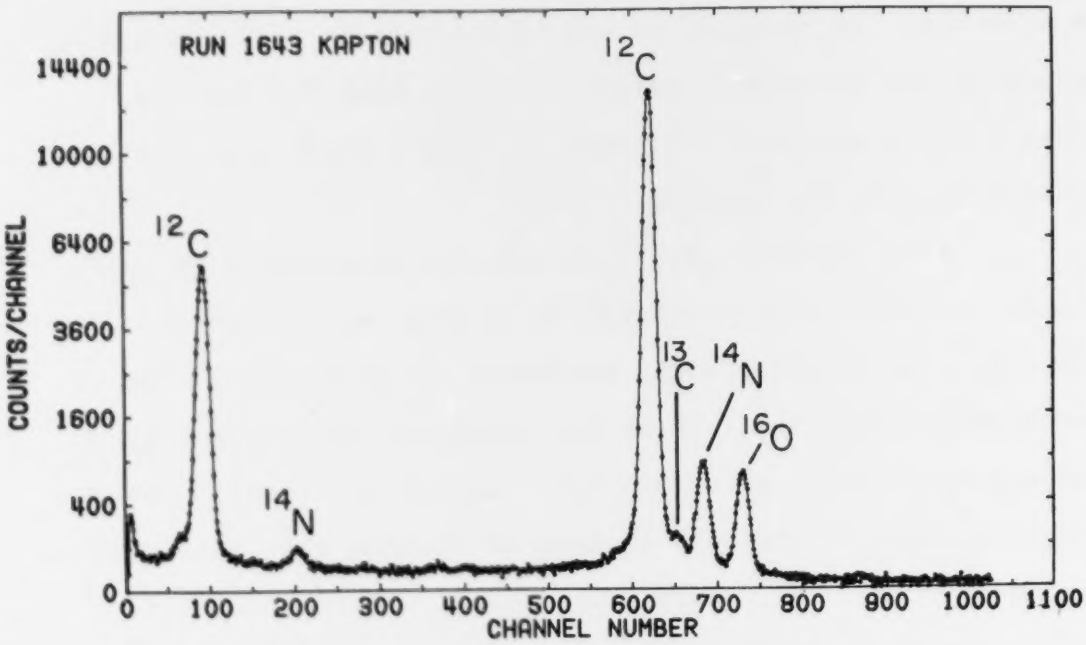


Figure 8. Calibration spectrum using the plastic Kapton.

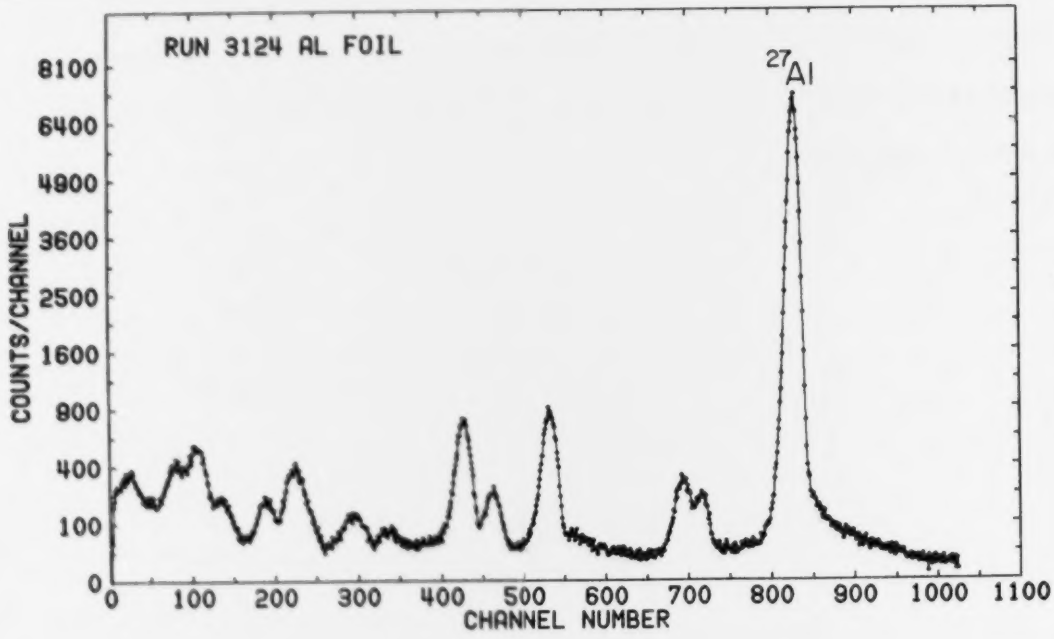


Figure 9. Calibration spectrum from an aluminum foil.

as possible. It consists of only two cards to define starting values of the non-linear parameters, one card for the run numbers to be analyzed and cards to select which elements are to be used from the library.

With insights gained during the development of SCAT, initial thoughts have developed on an even more powerful approach. In order to allow variation in peak shapes (due to the detector or samples which are thick or non-uniform) it appears feasible to integrate the Gaussian distribution over the line shape of the data instead of fitting the Gaussians to the spectrum. With this new approach a δ-function line shape results in a Gaussian peak but a rectangular or trapezodial line results in distorted peaks resembling those due to non-uniform or very thick samples. This method has been incorporated into an experimental program and initial results are most promising.

SECTION 7

TOTAL MASS DETERMINATION

Elements measurable by PESA represent most of the mass of a typical aerosol sample. PESA was used to determine the content of a filter-type sample and the total mass was compared to that determined gravimetrically.

Nuclepore filters 25 mm in diameter of 0.4 μm pore size were used. From 4 to 7 liters/minute was drawn through a circular spot on the filter 8 mm in diameter for 24 hours. Flow rates were measured every hour and the total volume of air sampled was calculated.

The filters were weighed on a Mettler balance accurate to ± 5 μg in a controlled (relative humidity 50%) atmosphere before and after the samples were taken. Before each weighing the samples were allowed to equilibrate for at least 12 hours in the controlled atmosphere. The total mass of particulate matter collected was then obtained by subtraction.

The samples were placed in a vacuum chamber and irradiated with 16 MeV protons. The scattered protons were detected at 120° laboratory angle. The resultant spectra were fitted using an interactive program which used a straight line for the background and assumed the peaks to be Gaussian. Yields were obtained in this manner for spectra taken on and off the spot

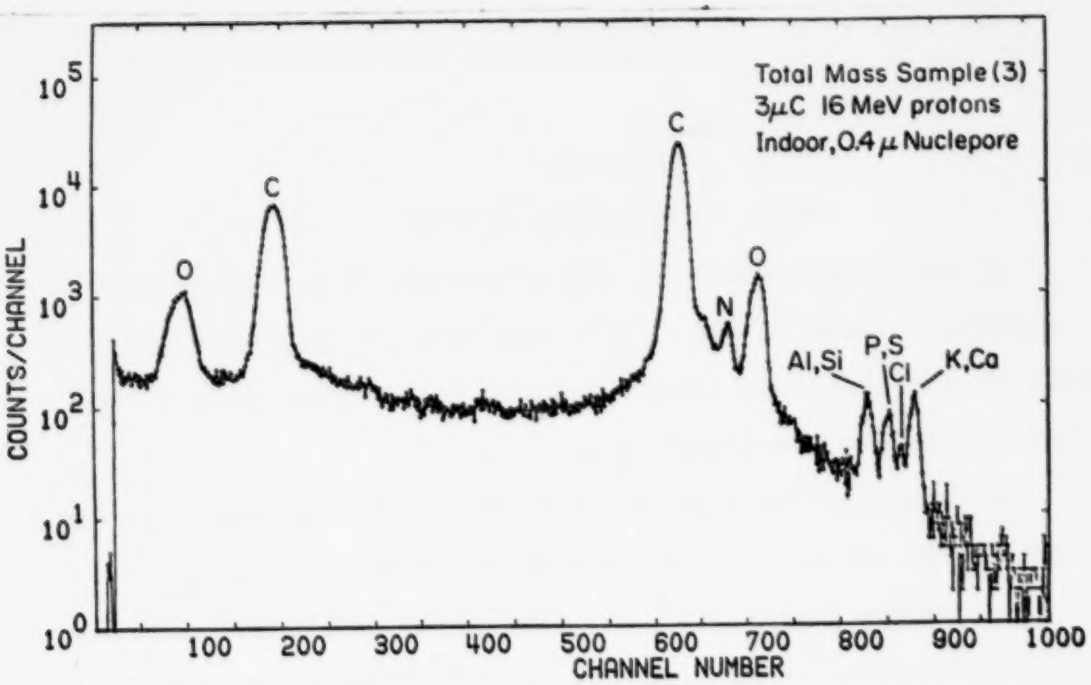


Figure 10. Scattering spectrum for an indoor aerosol sample.

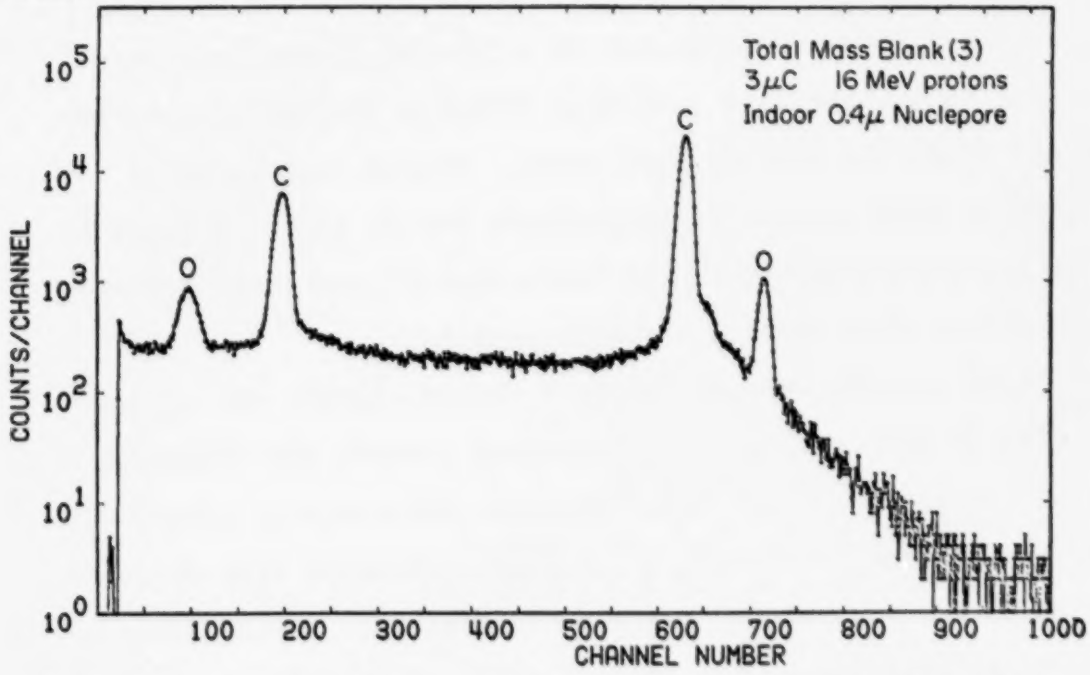


Figure 11. Background scattering spectrum taken a few millimeters distant from the spectrum of Figure 10.

containing the collected particulate matter. The difference thus represents yields from the aerosol particles only. A library of absolute cross section given in terms of counts per $\mu g/cm^2$ was used to calculate the cross sectional density.

Scattering spectra for a 24 hours indoor air sample from the Physics Department machine shop are shown in Figure 10 (beam on sample) and Figure 11 (beam on filter immediately adjacent to sample). Large peaks are seen corresponding to elastic and inelastic scattering ^{12}C and ^{16}O. In addition peaks due to ^{14}N, ^{27}Al, ^{28}S, $^{35,37}Cl$, ^{39}K and ^{40}Ca may be quantitatively evaluated. The total mass (see Table 2) observed by proton scattering was 647 µg while gravimetrically 998 µg was measured. From past experience we would estimate that the unobserved elements (hydrogen and elements above calcium) would contribute about 86 µg to make a total of 733 µg by summing weights of individual elements. The differences of 998-733 µg may be attributable to water loss when the sample is placed in vacuum, but further work is needed to clarify this situation.

Comparison of the weight of a sample before and after bombardment was hampered by the necessity of gluing the filter to a holder before irradiating it. Further experiments might be able to circumvent this difficulty.

TABLE 2. MASSES OF LIGHT ELEMENTS FOR AN INDOOR INDUSTRIAL FILTER SAMPLE

ELEMENTS	MASS (μg)	%	NET YIELD
C	330±2	45	125,833
N	36±0.5	5	6,266
O	109±3	15	8,834
Al-Si	143±4	19	1,137
S	14±0.5	2	837
Cl	5±0.2	<1	556
K-Ca	10±0.3	1	1,233
Estimated mass of unobserved elements	86	12	

SECTION 8

CARBON DETERMINATION

Determination of the amount of carbon in a sample presents special problems. Most filters and backing materials used in air sampling work contain carbon as a major constituent. In order to minimize the error due to background subtraction, either the filter must be very heavily loaded or the filter itself must be made thinner. Heavy loading is an unattractive alternative since in x-ray analysis it makes self absorption corrections difficult to impossible for softer x-rays. On the other hand, thinner filters are within the means of present technology and may even be purchased on special order. Still another approach would be the use of special low carbon content filters for separate carbon determinations; however, the addition of a separate system for a single element appears unwarranted if the thinner filter method is developed.

Proton scattering spectra for two types of thin commercially available filters are shown in Figure 12. Both spectra were measured for the same number of incident protons ($Q = 2\mu C$) and show that the Millipore contains less carbon than the Nuclepore. On the other hand, its use in aerosol analyses is made far less attractive by its considerable nitrogen content. A similar situation is also found for possible impaction surface

Nylon. As shown in Figure 13 the Nylon contains sufficient nitrogen as to make it an unattractive substrate when nitrogen determinations are desired.

Examples of carbon measurements on aerosol samples are shown in Figures 14 and 15. Figure 14 is the scattering spectrum for 16 MeV protons incident upon a single-orifice impactor sample (particles $\geq$ 4μm aerodynamic diameter) for 1.1m^3 of air from the coastal region north of Los Angeles, California. The numbers above each of the peaks are the masses of the elements in micrograms per cubic meter of air. In this case, with a paraffin coated polystyrene backing ($\simeq$ 100 μg/cm^2), the carbon in the sample represents 26% of the carbon present. The amount of carbon in the backing was measured by bombardment of the backing at a location about 2mm away from the sample.

A spectrum resulting in determination from bombardment of a deposit on a carbon Nuclepore filter is shown in Figure 15. In this case analysis of a six-hour summertime sample from downtown St. Louis, Missouri, yields a carbon value of 16% of the total carbon present and a ±14% statistical error. Another feature of interest in this figure is the overall broadening of all peaks which is a measure of total mass loading.

Figure 12.

PESA spectra for Nuclepore and Millipore filters.

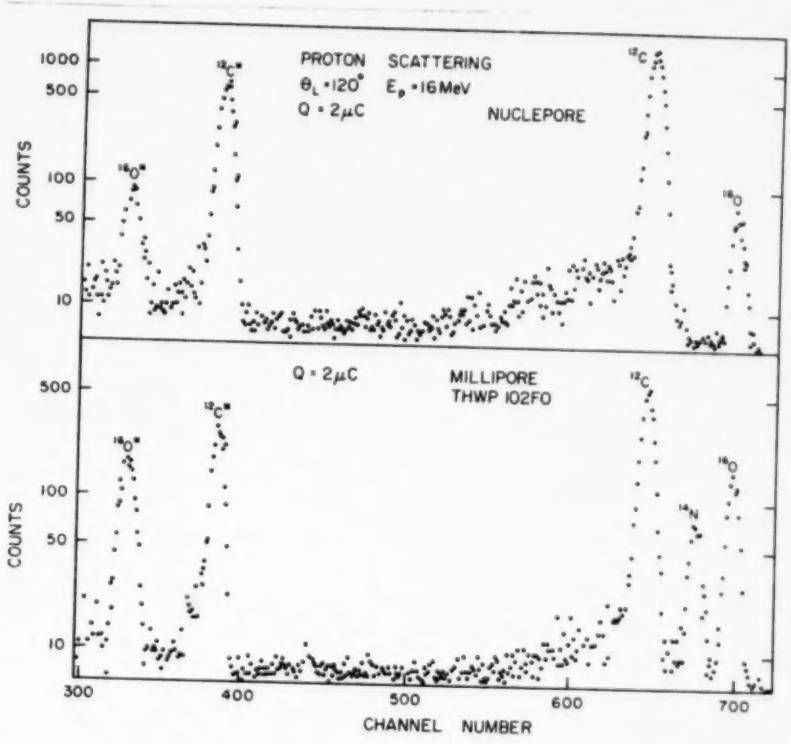
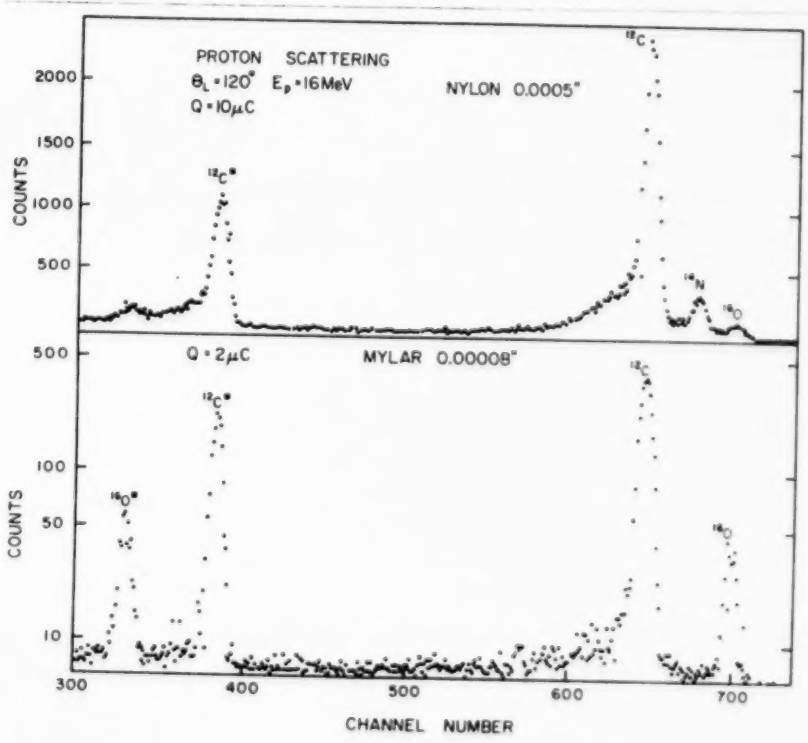


Figure 13.

PESA spectra for possible impactor surfaces - Nylon and Mylar



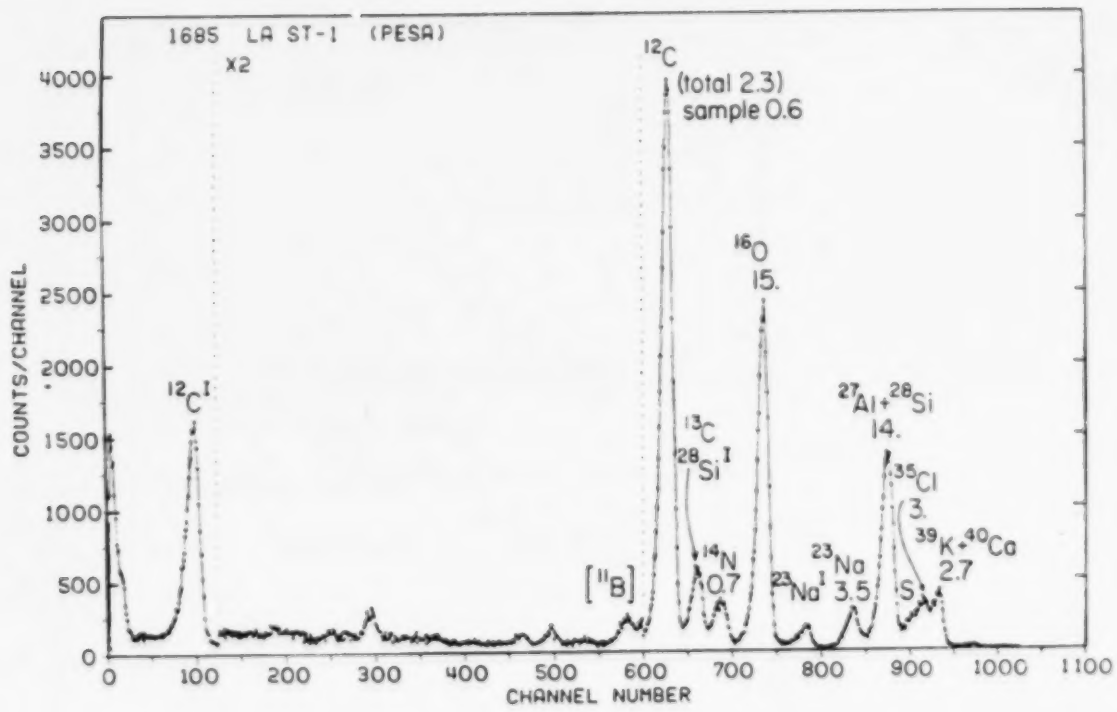


Figure 14. PESA spectrum for an impactor sample which allows quantitative determination of aerosol carbon.

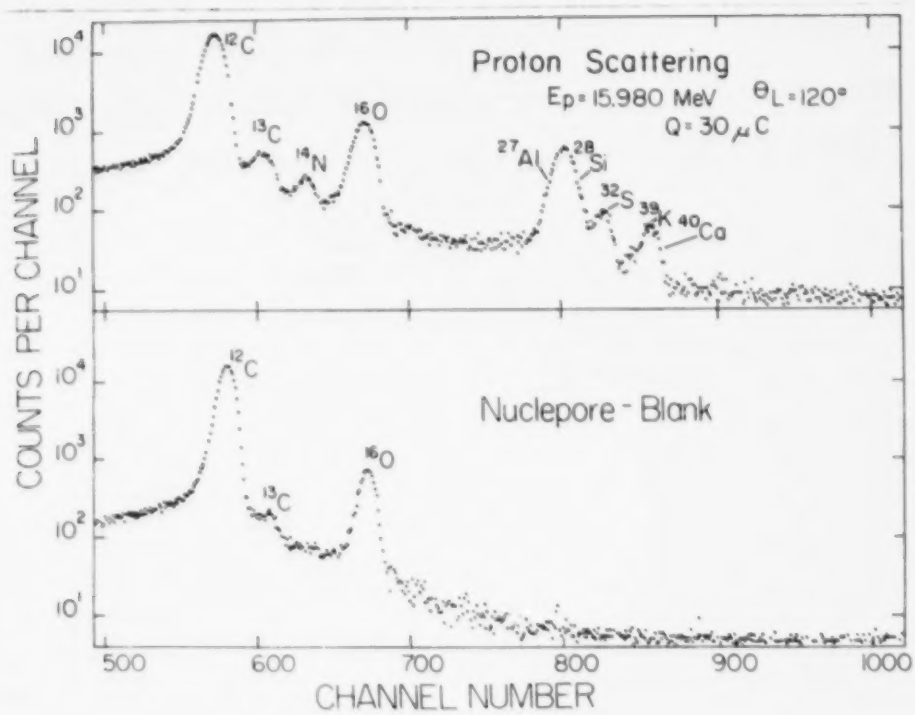


Figure 15. Spectrum for Nuclepore filter sample of sufficient thickness to permit carbon content determination.

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PROTON SCATTERING FOR ANALYSIS OF ATMOSPHERIC PARTICULATE MATTER*

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Proton scattering has been applied to the problem of elemental quantitative analysis of air particulate matter. Elements up through chlorine may be resolved using 16 MeV protons incident upon targets up to about 1 mg/cm^2 in thickness. Using the FSU Super FN Tandem Accelerator and a large area solid state proton detector, an analysis can be performed in several minutes. Combination of this technique with proton induced X-ray emission analysis provides a means of quantitative analysis for all elements. These accelerator based methods are being applied to studies of the composition of air particulate matter in diverse locations such as St. Louis, Mo.; Los Angeles, Ca.; several cities in Florida; and Bermuda.

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(proton scattering; quantitative analysis; air particulate matter)

Introduction

Direct measurement of the most abundant elemental constituents of atmospheric aerosol particle size fractions is important in relating aerosol particle physics theory to the variation of chemical composition with particle size. The former depends on physical interactions leading to particle coagulation and removal from the atmosphere, which are functions of particle mass,[1] and the latter is important in describing the transport of specific chemical substances in the atmosphere, many of which are of practical public health importance.[2] The direct measurement of the most abundant constituents, carbon, nitrogen, and oxygen, however, is difficult by most analytical techniques and in practice is almost never attempted in atmospheric research requiring large numbers of separate elemental analyses. Therefore, full advantage has not been taken of our present understanding of the physics of aerosols in accounting for the occurrence of chemical components of aerosol particles.

The present research is directed toward developing a sensitive and rapid technique for determining the light elements up to sulfur and chlorine in non-volatile components of aerosol particle size fractions by proton elastic scattering analysis, PESA.[3-5] Elements sulfur and heavier can be determined by proton induced X-ray emission, PIXE,[6-8] and the two methods in combination should provide a determination of all elemental constituents which contribute significantly to the total aerosol particle mass. The present paper presents evidence that this approach is feasible, and the two techniques can be applied to the same atmospheric samples by proton bombardment in a Van de Graaff accelerator.

Experimental

The experimental arrangement is similar to that used in our previous reports.[3-5] A collimated proton beam of 16 MeV is used as an optimum of high enough energy to provide resolution of protons elastically scattered by isotopes of adjacent elements up to chlorine and of low enough energy to be stopped completely in the available Si detector of 1500 micron depletion depth. The detector used in the present study is 6 mm x 30 mm active area collimated by a 1 mm elliptical curve running the length of the detector, so as to accept a narrow range of backscattered proton energies from each target nuclide at the 120° detector angle and still have a large enough effective detector surface area to

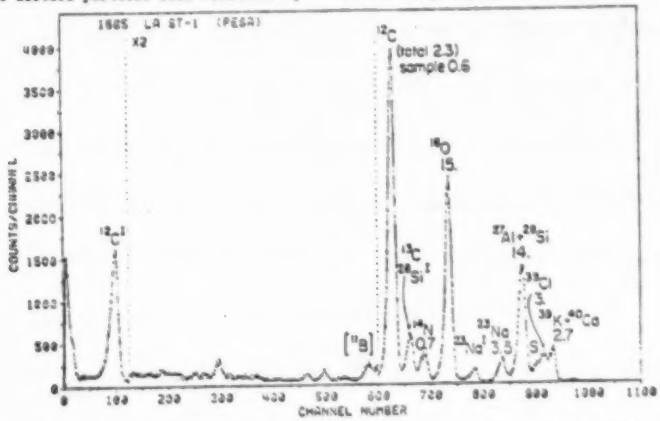

Fig. 1 Proton scattering spectrum for 16 MeV protons incident upon an air particulate sample from the coast north of Los Angeles, California. This sample was obtained from 1.1 m^3 of air using a single orifice cascade impactor. The numbers above each peak are the mass of that element in micrograms per cubic meter of air.

assure good counting efficiency for small aerosol particle samples in the target position. The detector is located outside the vacuum system of the scattering chamber, and scattered protons pass through a 1/4-mil (6.25 μm) Mylar window and about 2 mm of air before entering the detector, causing negligible loss of resolution in comparison with other factors in the arrangement.

Results

Figure 1 presents the elastically scattered proton spectrum from a sample of aerosol particles greater than 4 μm aerodynamic diameter collected during a 16 hour period along a coastal location near Los Angeles, September 1974. The sample is stage 1 of a cascade impactor[9] operating at a 1 liter/min air flow rate, representing 1.1 m^3 total air volume, and the sample is supported by polystyrene film of thickness ~100 $\mu g/cm^2$. Figure 2 is an X-ray spectrum produced by bombardment of the same sample with 3.75 MeV protons and detection in a Si(Li) detector. At the present time the PIXE procedure is precisely calibrated[8] permitting routine quantitative analysis, and the PESA procedure is undergoing calibration verification. The sample from stage 1 is large and has a diameter of about 2 mm and the beam was collimated to about 1.5 mm. Thus, not all of the sample was analyzed. The numbers

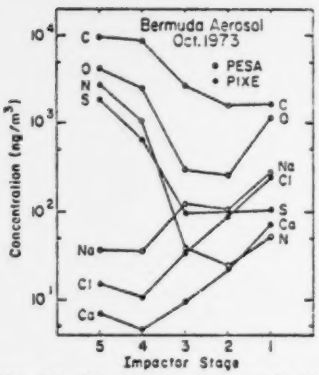

Fig. 3 Size fraction analysis of a Bermuda aerosol sample using proton elastic scattering analysis (PESA) for C,N,O, and S, and proton induced X-ray emission analysis (PIXE) for S,Cl, and Ca. Impactor stages 5 through 1 represent particles of equivalent aerodynamic diameters 0.25-0.5,0.5-1,1-2,2-4, and >4 μm, respectively.

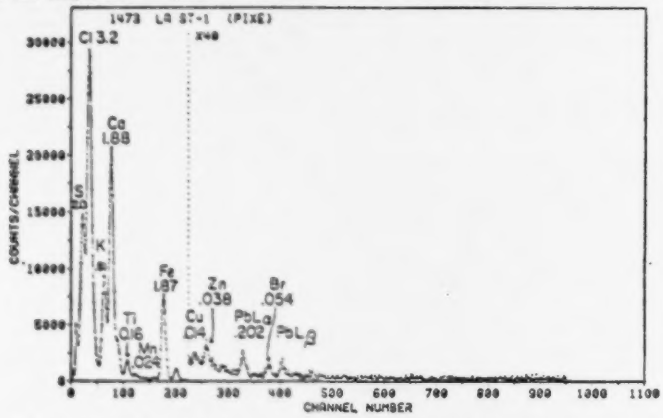

Fig. 2 Proton induced X-ray emission analysis of the same air particulate sample as shown in Fig. 1. Numbers above each peak are the mass of that element in micrograms per cubic meter of air.

of micrograms of each element given in Fig. 1 have been calculated after normalizing the PESA Ca + K value to that of PIXE, supposing the elements have the same distribution in the sample. It is seen that the sample size for PESA analysis is sufficient for detection of most elements from carbon to calcium and still small enough not to cause proton energy dispersion and loss of resolution. The sample size is also adequate for detection of about ten elements by PIXE.

Figure 3 presents the distribution of seven elements with particle size for a sample collected during a 72 hour period in October 1973 by cascade impactor from a tower in Bermuda.[10] This analysis, performed before the absolute PESA calibration was quantified, represents concentrations of S, Cl, and Ca by PIXE and concentrations of C, N, O, and S by PESA with normalization of S to the PIXE value all stages. Carbon values are approximate owing to uncertainties in polystyrene backing thickness. The particle size distributions show high large particle abundances for Na,Cl, and Ca, which may originate from sea water dispersion, and high small particle abundances for much of the N, S, and O, where composition of $(NH_4)_2SO_4$ is expected, and for some of the carbon. The combination of PESA and PIXE appears to be valuable for presenting enough elemental data to suggest chemical composition relationships such as these. PIXE alone would be insufficient.

Because of the special interest in measurements of nitrogen and sulfur related to the atmospheric chemistry of these elements, test bombardments have been carried out on targets which could serve as standards. Figure 4 shows the scattering spectrum for Kapton film, a material with a precisely known atomic ratio O/N = 2.5. The spectrum is simple and the elements are clearly resolved and can be readily analyzed by suitable computer programs. This material provides a convenient means to determine the relative N/O

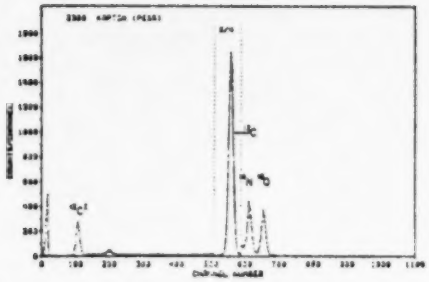

Fig. 4 Proton scattering spectrum for 16 MeV protons incident upon a 7.5 μm thick Kapton film.

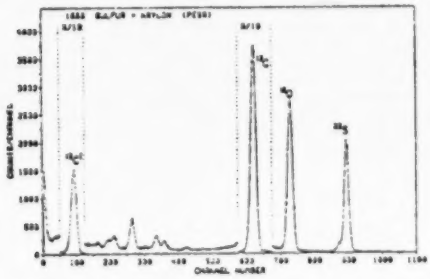

Fig. 5 Proton scattering spectrum for 16 MeV protons incident upon a sulfur target. The target was prepared by vacuum evaporation of elemental sulfur onto a Mylar backing and then over sprayed with Krylon to stabilize the sulfur to bombardment in vacuum.

scattering cross sections. Figure 5 shows the scattering spectrum for elemental sulfur on Mylar, with Krylon binder. The elastic scattering cross section for sulfur is dominant over lower energy inelastic proton groups in the spectrum. Our identification of peaks between channels 100 and 600 is not yet complete, but a few inelastic sulfur scattering peaks are apparently present and may be useful in quantitative resolution of spectra from complex mixtures as may be encountered in analysis of environmental samples. Current emphasis on high quality analyses of particulate sulfur in atmospheric samples, because of its pollution significance, makes it desirable to have alternate methods for sulfur determination. PESA and PIXE can both be applied to sulfur determination in the same samples.

High quality elemental analyses may be produced providing the proton scattering cross section is not highly sensitive to variables in a routine procedure and providing that variations in sample composition and thickness do not degrade the spectrum to the point of not being able to resolve the elemental constituents. As exemplified by Fig. 1, impactor sampling time may readily be chosen for obtaining a sample of size large enough for detection of elements by PESA and small enough to permit their resolution. It should be pointed out that thick samples tend to cause proton energy dispersion, not proton particle loss, and some dispersion can be tolerated if adjacent energy peaks can be resolved. In contrast, PIXE and any other X-ray methods for elemental analysis are vulnerable to X-ray attenuation at low X-ray energies, and this makes determination of elements lighter than sulfur uncertain if the required sample self-absorption corrections are large. Thus, in many practical cases, determinations of elements in the region of sulfur by both PIXE and PESA offer a decided advantage over determinations by one method alone.

In order to define the sensitivity of the PESA method to instrumental variables, measurements of effective cross section with angle and proton energy have been made. Figure 6 shows how the relative cross section varies with scattering angle for ^{12}C, ^{16}O, and ^{32}S. (These are relative values only. The variation of effective cross section at 120° with mass number of nuclides ^{7}Li to ^{40}Ca has been given in Fig. 9 of reference 5.) Figure 6 indicates that the sulfur cross section varies imperceptibly over a broad angle interval from 100° to 135°, oxygen has a gentle minimum centered about 118°, and carbon decreases almost monotonically with angle from 100° to 135°, being relatively flatter around 120° than angles greater or less than this. For convenience in our experimental arrangement and for the least practical sensitivity to variations in scattering angle, we have chosen 120° for most of our further calibration experiments. This choice of angle also affords a relatively high carbon cross section and permits precise carbon measurements where subtraction of backing material contribution is required. We also note that more forward angles suffer from apparently less satisfactory peak to background ratios, and the peaks are kinematically more closely spaced. These and other practical considerations for the resolution of elemental constituents in environmental samples indicate that the optimum angle chosen for analysis is not a trivial problem and should be explored with great care. At present, our choice of 120° appears to be a good one.

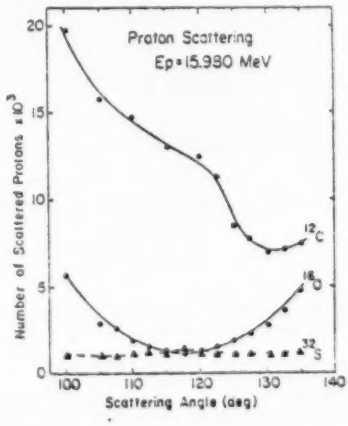

Fig. 6 Differential cross section in arbitrary units versus scattering angle for three isotopes. The lines through the points are guides for the eye.

Figure 7 shows relations calculated which influence the resolution which can be achieved for ^{12}C and ^{35}Cl. The angle subtended by the detector is determined by the width of the elliptical curve which forms the collimator of our detector face, currently about 1°. Since the intrinsic detector resolution is in the region of 40 keV, it is desirable to keep additional energy dispersion due to detector angle well below this value. This is especially true if resolution of ^{27}Al and ^{28}Si is to be achieved, as we consider necessary in atmospheric aerosol studies.

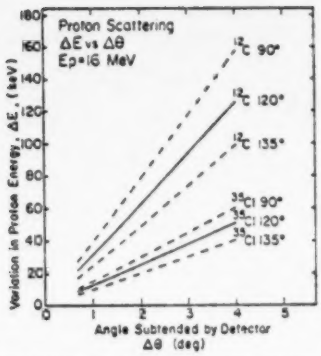

Fig. 7 Variations in scattered proton energy versus angle subtended by the proton detector. In the analysis system at FSU, angles between 1 and 2 degrees are employed.

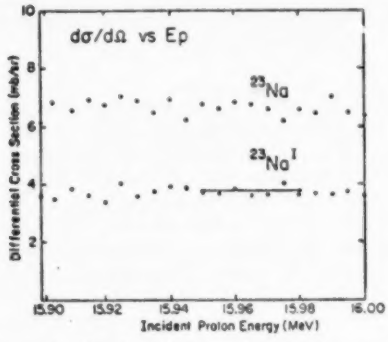

Fig. 8 Excitation functions for the ground and first excited states of ^{23}Na over the range of interest for the FSU analysis system. The lack of structure is desirable in that quantitative analyses do not depend upon sample thickness. The line indicates 30 keV, the maximum sample thickness analyzable with good resolution.

Finally, Fig. 8 shows the differential scattering cross section as a function of proton energy for ^{23}Na as measured from a 60 μg/cm^2 Na Cl sample. The uncertainty in the repeatability of the proton energy scale was ±10 keV. Data for the two major peaks observed in the sodium spectrum, elastic scattering from the ground state and inelastic scattering to form the first excited state, are given for a range of energy. This range is several times greater than we anticipate will be caused by extreme variations in sample thickness which can be accepted and still give the energy resolution required for a successful analysis for individual elements. Normally, no thickness greater than that equivalent to a 30 keV energy loss would be accepted, and neither sodium cross section is found to vary over this range. Also, it is seen from Fig. 8 that tedious energy calibration procedures of the incident proton energy are not necessary for sodium measurements. Clearly, such tests must be carried out for every element for which analysis is attempted. For those we have completed to date, similar results have been found, indicating no difficulties are foreseen due to cross section sensitivity to this effect. It is also fortunate that the ratio of cross sections for the elastic and inelastic groups of scattered protons from sodium is constant with energy, because then both groups can be used in the quantitative analysis for sodium in complex mixtures by straightforward computer fitting programs.

Conclusions

Experiments performed to date indicate that proton elastic scattering analysis can be a practical, rapid, and sensitive means of elemental analysis when applied to atmospheric aerosol samples. It has inherent simplicity, relative freedom from interference between elements present in the sample, and potential for automated nondestructive analysis. In combination with PIXE, PESA has the capability for determining all elemental constituents of aerosol samples that contribute significantly to the total aerosol mass, a capability which is unique in contrast to alternative analytical techniques. Future research and development of PESA should be directed to detailed cross section measurements of the nuclides of interest over the range of variables of energy, angle, and other parameters encountered in practical elemental analysis. An effort should be made to develop computer hardware and software which will automate the procedure so that analyses can be carried out in minutes or less of time and data can be handled readily for interpretation. Finally, the PESA technique should be field tested extensively so that relationships in elemental composition of environmental samples revealed by the technique can be evaluated. Such evaluations may indicate directions for further improvement of the technique.

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REX – A COMPUTER PROGRAMME FOR PIXE ANALYSIS*

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The implementation of a physics-based model for non-linear least-squares analysis of proton-induced X-ray emission spectra via a Fortran programme REX is discussed. The modelling of distinct spectral components and of the physical effects involved is briefly discussed. Results are presented in graphical and tabular form. The limitations of the present model are discussed and future refinements indicated.

1. Introduction

Proton-induced X-ray emission analysis (PIXE) has been shown to be a fast, inexpensive, reliable and convenient method for routine multi-elemental trace analysis[1]). The main divisions in such an analysis are: sample preparation and bombardment and decomposition of the measured pulse-height spectra. Intense work is going on in all these fields to find suitable, time-saving sample preparation techniques, to build bombardment and data-taking systems which are fast, reliable and automated and to develop inexpensive, reliable and automated computer programmes for resolving PIXE spectra. Kaufmann and Akselsson[2]) and Kaufmann et al.[3]) have earlier described versions of a computer code, REX, based on a model of the physics in PIXE-analysis. This report describes the current version of REX, some results obtained with it and a discussion of further improvements which can be made.

The parameters of the model are found using a least-squares minimization based on a technique developed by Kaufmann[4]).

2. The model

The radiation environment due to the photons present during proton bombardment of a sample may be deduced from the pulse-height spectra obtained from a Si(Li) detector. The photon radiation spectrum consists of discrete quanta due to characteristic X-rays and a continuum. The continuum proper has its origin in two phenomena: (1) bremsstrahlung of secondary electrons and of protons[2,3]) and (2) Compton-scattered electrons from high-energy X-rays and γ-rays which originate in or near the sensitive volume of the detector. For typical samples, the bremsstrahlung component is dominant: however, the sample thickness and composition and the amount of absorptive material between the sample and the detector can alter the relative contribution of the Compton electron component. To the first order, both phenomena scale with sample thickness and, while the bremsstrahlung component will be attenuated by any absorptive material present, the Compton electron component will not.

The putative Compton electron component is modelled in a fashion which implicitly allows for phenomena such as bremsstrahlung escape and backscattered photoelectrons. Both of these contributions to the continuum are more properly modelled in the detection process. Preliminary attempts at implementing a more precise model for these components will be deferred to a later section. The model discussed here does not include the silicon escape peaks for the characteristic radiation: inclusion of these in the model presents some difficulty as will be discussed later.

For the case in which the size of a thin sample is smaller than the area of the proton beam, the yield of a characteristic K X-ray transition is given by

$$\Sigma = nN\sigma\omega k T_1 T_2 \varepsilon\Omega/(4\pi), \qquad (1)$$

* Research supported in part by US Environmental Protection Agency, Grants R-803913 and R-803887.

where n is the proton flux in particles per cm^2, N is the number of atoms of the elements, σ is the ionization cross section for the K-shell, ω is the fluorescence yield for the K-shell, k is the branching ratio for the emission of the characteristic X-ray, T_1 is the transmission between the sample and the detector, T_2 is the mean transmission for X-rays through the sample itself, ε is the detector efficiency and Ω is the solid angle subtended at the detector by the collimator.

The proton flux, n, is deduced from the dead-time-corrected integrated charge and the values for σ, ω, and k are taken from refs. 6, 7 and 7 respectively.

The factors T_1, T_2 and ε in eq. (1) depend on the X-ray energy as do the continuum components to be discussed later. Thus, it is most convenient to express the model in terms of "equivalent" X-ray energy rather than as pulse-heights. The "equivalent" energy corresponding to a particular pulse-height is taken here to be the energy of fictive monoenergetic X-rays which would give their full-energy peak at that pulse-height. The parameters of the transformation of the spectra from pulses/channel to pulses/energy interval are included in the least-squares fit.

The form of the transformation depends on the characteristics of the pulse-height analysis system. For optimum speed, a linear calibration is crucial and in this case the transformation is given by

$$E = p_1 + p_2(x - j_0), \tag{2}$$

where p_1 and p_2 are parameters, x is the channel number and j_0 is a fixed channel number chosen to optimize the calculational procedures.

When applied to a thin sample on a thin backing, the model gives the following expression for the yield of pulses per energy unit:

$$f(P,L,E) = \mathrm{CON1}(P,E) + T_1(P,E)\cdot T_2(P,E)\cdot \cdot \mathrm{CON2}(P,E) + \sum L(I)\cdot T_1(P,E(I,J))\cdot \cdot T_2(P,E(I,J))\cdot \mathrm{PEAK}(P,E(I,J)), \tag{3}$$

where f is the number of pulses per energy unit, P is an array of non-linear parameters, L is an array of linear parameters, $T_1(P,E)$ is the transmission through absorbers external to sample, $T_2(P,E)$ is the mean transmission through the sample material, CON1(P,E) is the continuum unaffected to the first order by absorption effects such as, e.g., from Compton scattered electrons, CON2(P,E) is the continuum affected by absorption such as, e.g., bremsstrahlung from secondary electrons and PEAK$(P,E(I,J))$ is the characteristic X-ray line shape convoluted with a detector response-function.

The indices I and J refer to the atomic number of the element, e.g. Fe, and to specific characteristic X-ray transitions of the element, e.g. $K_{\alpha 1}$, respectively. The parameter arrays, P and L, are found by minimizing the function

$$\chi^2 = \sum_i w_i(y_i - f_i\,\mathrm{d}E/\mathrm{d}x)^2, \tag{4}$$

where y_i is the number of pulses in channel i, $w_i = 1/y_i$ if $y_i > 0$, otherwise $y_i = 1$ and $\mathrm{d}E/\mathrm{d}x$ is the derivative of the transformation from channel-space to energy-space. In the case of a linear transformation [eq. (2)], the component $\mathrm{d}E/\mathrm{d}x$ is folded into the linear parameters and is thus included in f.

It is the simultaneous fitting to all the model parameters describing the entire pulse-height spectrum which distinguishes the present approach from others. As is illustrated by the fitted data shown later, this approach provides a versatile solution to such common problems as element interferences and the use of unorthodox absorption schemes.

3. Discussion of the components in the model

3.1. Characteristic X-ray transitions

Although the detector response to a X-ray transition is better described as the sum of a Gaussian and a low-energy electron backscatter tail[8]), to minimize computing-time, we have chosen to approximate the system response by a Gaussian without tails. The full width at half maximum (fwhm) of this distribution is dependent on the energy of the detected radiation. In REX, this dependence is taken to be of the form

$$\mathrm{fwhm} = p_3[E/E_0]^{p_4}, \tag{5}$$

where p_3 and p_4 are suitable parameters and E_0 a reference energy which serves the same purpose as j_0 in eq. (2).

The intensity of the X-rays from each element are parameterized with a single amplitude and the different transitions for each element are scaled to this parameter using known relative intensities. This procedure lessens the ambiguity in dealing with interfering transitions from different elements. Transitions from a particular element are included individually if they are separated by more than 50 eV.

Obtaining reliable measurements of the elemental masses based on the yield of K X-rays depends mainly on the accuracy of the elemental standards. For L X-rays, the relative intensities are significantly dependent on the proton energy. Thus, elemental standards for L X-rays have to be analysed at the same energy as the samples. For thick samples, these variations in the relative transition probabilities give rise to complications which cannot yet be resolved using REX.

3.2. Continuum

The continuum component not affected by first-order absorption, CON1, is mainly caused by Compton scattered electrons passing through the sensitive volume of the detector. Other processes are, however, also involved and it is not straightforward to model this component from basic physics of the process. The following empirical expression has been found to give good fits:

$$\mathrm{CON1} = p_{11}/E + p_{12} + p_{13}z + p_{14}z^2 + p_{15}z^3, \quad (6)$$

where $z = x - j_1$, x is the channel number and j_1 a reference channel chosen to give a suitable range for the numbers in the calculations. In spectra having no peaks above 15 keV, the parameters p_{13}, p_{14} and p_{15} are held fixed at zero.

The bremsstrahlung component has been thoroughly investigated[5]). However, to save computing-time, we have used the approximation

$$\mathrm{CON2} = \exp(-p_6 z)\cdot(p_7 + p_8 z + p_9 z^2 + p_{10} z^3), \quad (7)$$

where $z = x - j_1$, x is the channel number and j_2 a reference channel. Empirically this expression is found to give good fits.

3.3. Transmission

In earlier versions of REX[2,3]) four nonlinear parameters were used to describe the transmission through the sample itself and through external absorbers. Since each nonlinear parameter adds significantly to the computing-time and since three of these parameters did not vary between runs, we have remodelled the transmission factors.

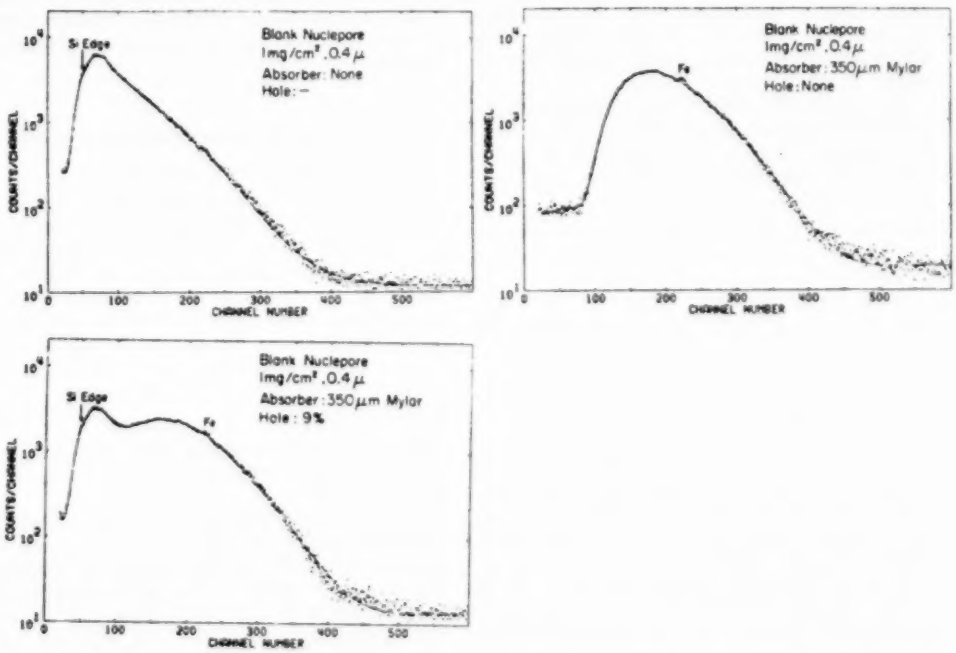

Fig. 1. Fits to proton induced X-ray emission spectra obtained from bombarding nominally blank Nuclepore filters using a variety of detection schemes. Note in particular the fit to the spectrum obtained by using an absorber with hole (bottom).

The external absorber is a multi-component absorber consisting of foils to maintain vacuum in the sample chamber and the detector housing, of the gold layer and the dead-layer of the detector, of air and of an optional absorber. The "transmission" through this system is modelled by

$$T_1 = \varepsilon T_{opt} = \exp(aE^b)\,[1 - \exp(cE^d)]\,T_{opt}, \qquad (8)$$

where ε is the detector efficiency and T_{opt} the transmission through an optional absorber. The contants a, b, c, and d in the expression for the detector efficiency[9]) are initially obtained by a least-squares fit and are then held fixed.

The mean transmission through the sample itself is modelled by

$$T_2 = [1 - \exp\{-\mu(E)p_s\}]/[\mu(E)p_s], \qquad (9)$$

where $\mu(E)$ is the absorption coefficient of the sample matrix. For certain standard matrices, $\mu(E)$ is tabulated in REX.

The optional absorber may be a solid Mylar sheet. However, in the usual case with samples predominantly composed of low Z elements but with traces of high Z elements, an absorber with a small hole may be an optimum. This type of selective absorption is easily introduced without adding more parameters by writing

$$T_{opt} = (1 - H)\exp\{-\mu(E)\,d\} + H, \qquad (10)$$

where H is the fraction of the solid angle Ω subtended by the hole, $\mu(E)$ the absorption coefficient as a function of the X-ray energy E and d the thickness of the absorber.

4. Results

The coding of the model in the Fortran programme REX has been undertaken with speed of calculation and memory requirements being of primary concern. At present the programme is compiled in 42k of memory in a Datacraft 6024/3 computer. Execution time per spectrum evaluation varies between 20 and 180 s depending on the quality of the starting parameters and the number of fixed parameters.

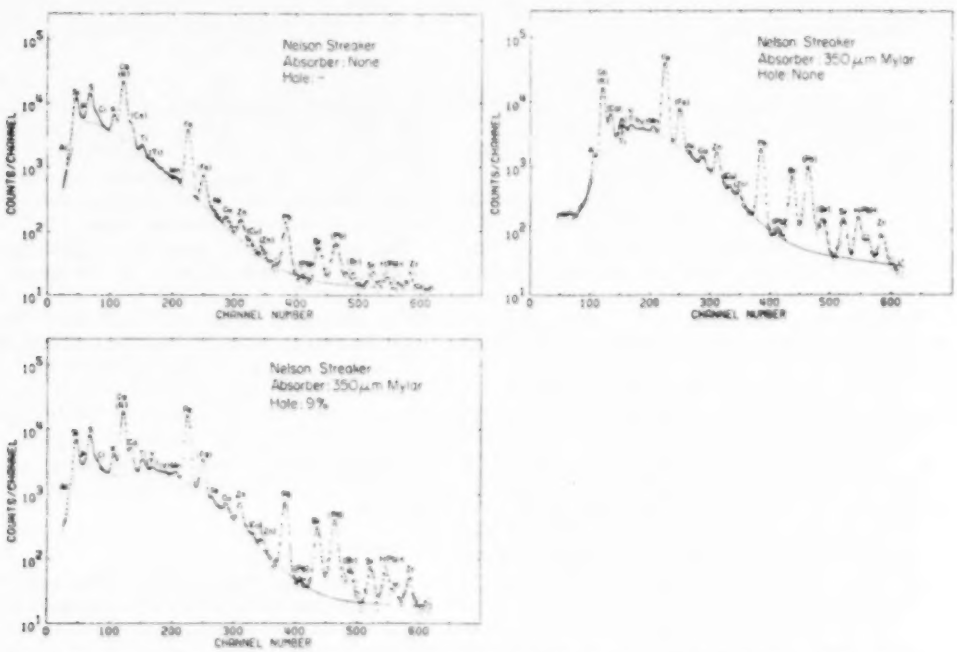

Fig. 2. Fits to proton induced X-ray emission spectra obtained from bombarding an aerosol sample obtained with the Nelson Streaker. For quantitative comparison see table 1.

TABLE 1

Comparison of results from runs using different absorbers. The sample analyzed is from 2 m^3 air and the count rate in all three analyses was 1000 cps analyzed for 500 s each

Element	Absorber: None Hole: —			Absorber: 350 μm Mylar Hole: None			Absorber: 350 μm Mylar Hole: 8.9%		
	Amount (ng/cm^2)	Error (%)	MDL[a] (ng/cm^2)	Amount (ng/cm^2)	Error (%)	MDL[a] (ng/cm^2)	Amount (ng/cm^2)	Error (%)	MDL[a] (ng/cm^2)
Al	1914	53	205				2013	37	231
Si	6743	39	53				5740	32	59
P	426	40	36				203	36	40
S	1633	32	21				1314	30	24
Cl	233	23	18			1030	90	24	20
K	557	20	13	543	20	32	504	19	14
Ca	3300	19	12	3486	19	13	2893	19	11
Ti	133	17	11	165	17	6	135	16	7
V			11	12	25	5			7
Mn	24	20	11	33	16	3	26	16	5
Fe	1404	14	7	1625	14	2	1338	14	3
Ni	23	19	7	10	17	2	9	19	3
Cu	36	15	6	28	13	2	27	14	2
Zn	74	15	6	69	14	2	61	14	2
Pb	556	16	27	693	16	5	573	16	8
Br	120	14	6	119	14	1	110	14	2
Sr	41	19	10	44	14	2	42	14	2
Zr	45	21	15	26	15	3	30	15	4

[a] Minimum detection limit.

The quality of the present model may best be assessed by examining fitted spectra from a variety of detection and sample conditions. In this section, we present such an assessment.

The continuum model was tested by obtaining photon spectra from a nominally blank hydrocarbon filter material such as Nuclepore. In fig. 1 fitted spectra for data obtained using the three common absorption schemes in the aerosol research programme at FSU are shown. The continuum model provides a good description of the data in all three cases.

A test of the complete model on real data is presented in fig. 2. The data are from the proton bombardment of an aerosol sample obtained with a continuous filter sampler[10]. Once again the spectra were obtained using the three common absorption schemes and are from bombardments of the same spot on the filter. As a further illustration of the overall versatility and reliability of the analysis, the masses obtained for each element in the three analyses are tabulated in table 1.

Careful study of the figures and table 1 indicates some of the inadequacies of the present model. The silicon K-shell edge absorption affects the measured values of P, S, and Cl significantly. The fitted spectra deviate from the functional form of the data at both the lowest and the highest energies in the spectra. However, the analytical errors associated with these effects are comparable to the instrumental systematic errors.

The ease with which elemental interferences are handled is illustrated in fig. 3. In the upper part of the figure is displayed the result of a fit to a PIXE analysis of an aerosol sample from Chacaltaya, Brazil[11]) in which As has been omitted from the element request list. The fit for the Pb X-rays is seen to be very poor. The lower figure includes both As and Pb in the request list and the resulting fit is excellent. The element library and the simultaneous fitting of all model parameters greatly facilitates the correct accounting of element interferences.

5. Discussion

We have presented a status report describing the continuing development of a programme to obtain reliable quantitative measurements of trace elements using proton induced X-ray emission. The model used is based on the physics of X-ray

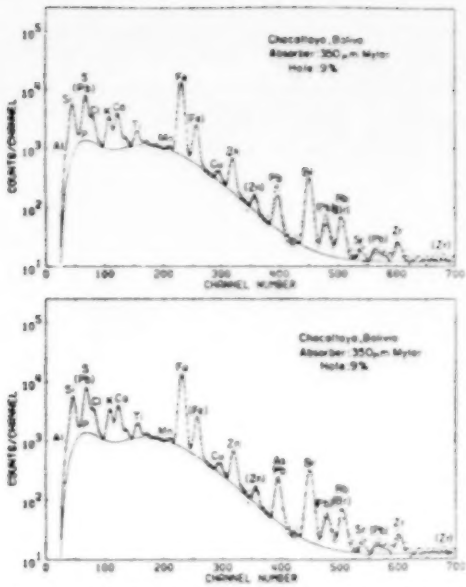

Fig. 3. Fits to a spectrum from an aerosol sample without (upper) and with (lower) arsenic in the request list.

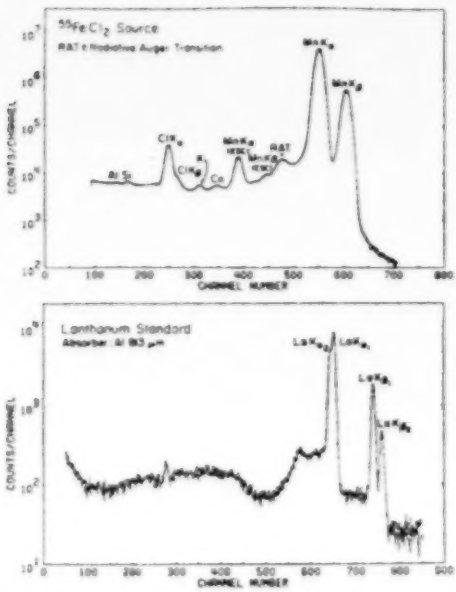

Fig. 4. Two spectra showing features which the current version of REX is unable to fit. These are silicon escape peaks (ESC) and radiative Auger emission (RAT) in the upper spectrum and the low-energy shoulders on the peaks and the broad bump between channels 150 and 500 in the other spectrum.

production and detection. The data presented attests to the overall suitability of the model and of its implementation.

Pointers to future refinements of the model are shown by the inadequate accounting of the continuum as can be seen in the fitted data in figs. 1 and 2. At present, the errors associated with these errors are comparable to the errors associated with the instrumentation and do not therefore greatly lessen the accuracy of the analysis.

Some of the difficult problems which must be solved are displayed in fig. 4. The upper figure is a spectrum from a long accumulation of the X-rays from a $^{55}FeCl_2$ source. The spectral properties which we do not explicitly include are (a) the Si K X-ray escape peaks and (b) possible radiative Auger emission[2]). Although we can, in principle, include the escape peaks in the present model, in practice the inclusion is made difficult by the excessive width of the escape peak compared to that of a full energy X-ray of the same energy. The radiative Auger transition is very weak [$\approx 0.5\%$ of the intensity of the K_α-transition[2])] and thus should only present an analytical problem when small amounts of a lower Z element are to be measured in the presence of an abundant interfering element of higher Z.

The lower part of fig. 4 shows a spectrum taken during proton bombardment of a La standard. The La L X-rays have been absorbed so that the detector response to the K X-rays can clearly be seen. In this particular case, the causes of the shoulders on the low energy sides of the peaks and of the rise of the continuum at energies below about channel 450 are not unambiguously known.

We hope to resolve some of these questions by measuring the detector response to monoenergetic photons obtained by single-crystal diffraction.

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LIGHT ELEMENT ANALYSIS BY PROTON SCATTERING

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A system for quantitative elemental analysis by proton scattering at 16 MeV has been developed. Samples of thicknesses up to 1 mg/cm^2 may be analyzed for the light elements up to Cl. Examples of spectra for atmospheric particulate matter and biological specimens are shown.

1. Introduction

Proton induced X-ray emission analysis (PIXE) may be used to perform quantitative analyses of any element on many types of samples. No single system design is optimum for measurement of all elements in samples ranging from very thin to infinitely thick to the proton beam. Using proton beams of the Florida State University Tandem Van de Graaff accelerator, we have developed an energy dispersive PIXE analysis system[1]) for thin solid samples (thicknesses up to approximately 1 mg/cm^2). Attenuation of the softer X-rays in both the sample and windows, limits the usefulness of our system to analyses of elements having $Z \geq 13$. Proton elastic scattering analysis (PESA) has been developed for light elements in order to complement our PIXE technique.

While quantitative PIXE analysis may be performed for even the lightest elements, absorption by the sample itself imposes severe limits on the useable thicknesses of solid samples. In planning our system primarily for determinations on air particulate matter, individual particle linear dimensions up to 10–50 μm were of interest. For selected elements the thicknesses needed to reduce the intensity of a beam of X-rays by one-half as a function of photon energy are shown in fig. 1. For particles in the 10 μm region attenuation is seen to be a major correction in quantitative measurements. For this reason proton scattering was investigated as a complementary method for analysis of light elements.

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2. Proton scattering analysis

A light element method to supplement PIXE analysis should possess similar characteristics and sample requirements as PIXE. Proton elastic scattering analysis has properties which make it quite complementary. It is absolute, multi-element, rapid, subject to automation and non-destructive of the prepared sample. Sample thicknesses up to about 1 mg/cm^2 may be used. Unlike the X-ray analysis in which too thick a sample attenuates but does not degrade the quality of the spectrum, PESA spectra exhibit loss of resolution which immediately signal that sample thickness is too large. Although nuclear scattering cross sections are several orders of magnitude smaller than those for X-ray production, comparable analysis times (min-

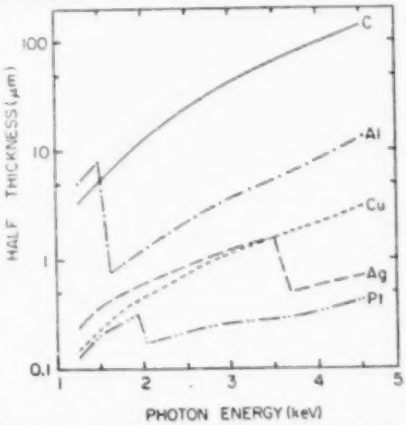

Fig. 1. Thicknesses needed to reduce the intensity of a beam of X-rays to half value as a function of photon energy for selected elements.

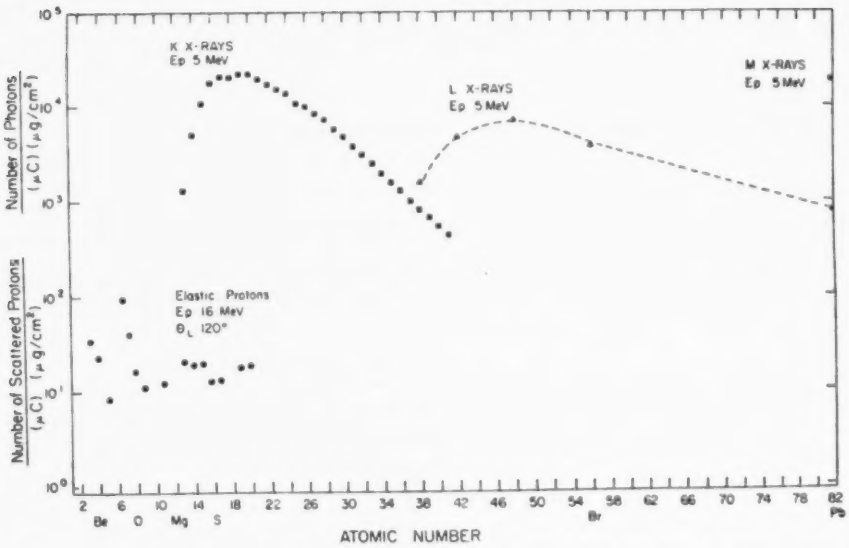

Fig. 2. Overall efficiency of the Florida State University combined PESA-PIXE quantitative analysis system.

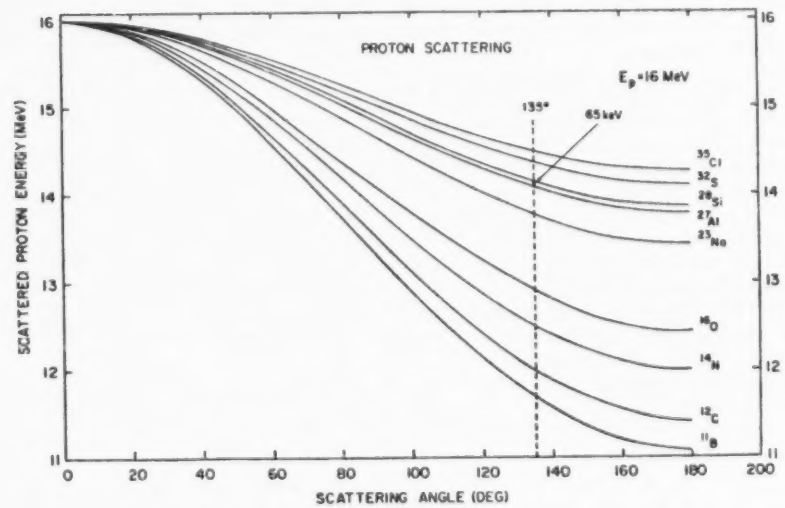

Fig. 3. Kinematics of 16 MeV elastic proton scattering for some of the light elements.

utes) are achieved on air particulate samples. This is in part due to the presence of larger amounts of many light elements. In fig. 2 the overall efficiency of the FSU system[2]) is shown. Only those elements for which the production cross section has been determined for our system are shown. The ordinate is not the cross section as usually defined but the readily useable number of outgoing particles per μC of incoming protons per $\mu g/cm^2$ of sample.

Values of elastic scattering cross sections are generally an order of magnitude higher than the inelastic cross sections. Thus elastically scattered protons were chosen for analysis rather than inelastic groups or the gamma rays accompanying inelastic scattering. Further choices of the incident proton energy and angle of detection were dictated by other considerations. An incident proton energy 16 MeV was selected on the basis of dependable accelerator operation (1 MV below maximum rated voltage), greater energy difference between adjacent mass nuclei, and smallest energy loss in the sample. In fig. 3 the kinematics of 16 MeV elastic proton scattering are presented. Selection of a rearward scattering angle is necessary for a sufficient energy difference to permit resolution of target mass 27 from mass 28. Assuming an overall system resolution of 30–40 keV is maintained, a scattering angle of 135° will result in a 65 keV separation to allow determination of both aluminum and silicon. From fig. 3 protons scattered at 135° from elements carbon through chlorine will have energies between 12 and 15 MeV and may be stopped in large area (300 mm^2) 1500 μm depletion depth detectors.

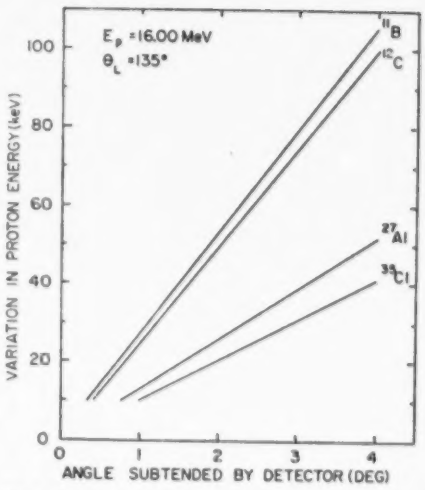

Fig. 4. Energy variation of scattered protons versus the angle subtended by the detector.

In the desire to attain the highest counting rate consistent with 30–40 keV overall resolution, the energy broadening contribution due to the angle subtended by the detector was calculated and is shown in fig. 4. At a scattering angle of 135° we utilize detector collimators which subtend 1°–2° in order to constrain this source of loss of resolution

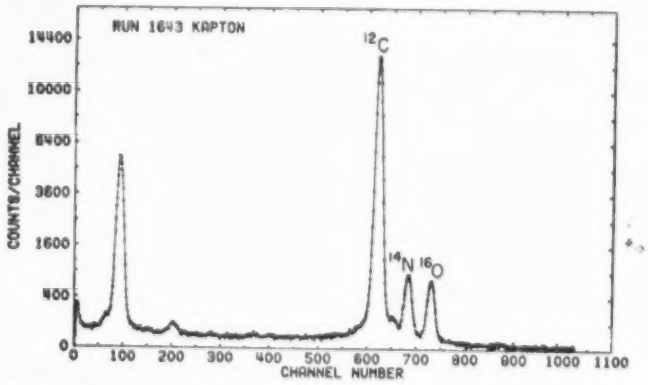

Fig. 5. PESA spectrum for Kapton plastic.

to about 20 keV. A further practical consideration is the mechanical problem of milling elliptically shaped collimators for large area detectors which subtend a significant fraction of the cone of equal energy outgoing particles. From the standpoint of the kinematics alone, the most extreme backward scattering angle approaching 180° is desirable. Mechanical problems of target chamber construction with detector outside the vacuum chamber influenced us not to use this approach. On the other hand the 90° scattering angle offers the possibility of the use of linear shaped collimators but at a cost of less kinematic energy separation of adjacent masses (see fig. 3).

3. A particular PESA system

One system has been developed at FSU using 16 MeV incident protons and detecting scattered protons at 120° with respect to the incident proton direction. Typical PESA spectra are shown in figs. 5 and 6. In fig. 5 the spectrum of Kapton plastic is shown. Referring to fig. 2 it may be observed that carbon and nitrogen are accentuated relative to oxygen at this scattering angle and incident energy. Thus a suitable evaluation computer code must be developed to account for the relative cross sections. Such a program is in the final stages of development and is closely patterned after our PIXE analysis program REX[3]). For exam-

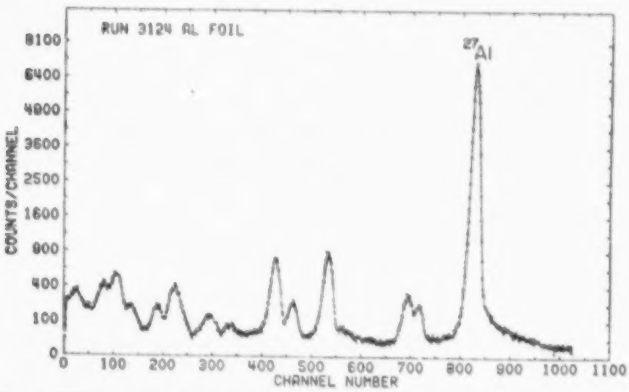

Fig. 6. PESA spectrum for the element Al. This is the most complex spectrum among those of the elements lighter than calcium.

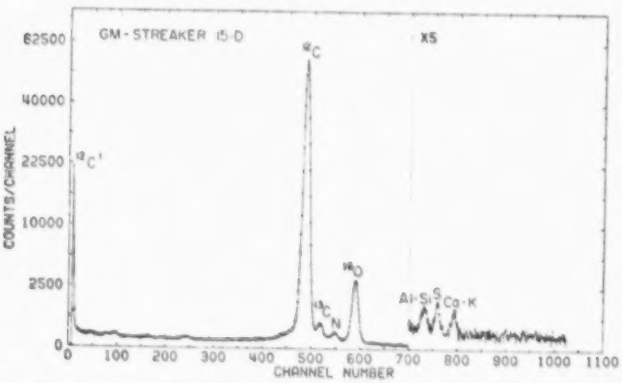

Fig. 7. PESA spectrum obtained by bombarding a Nuclepore filter particulate sample of relatively clean winter air from rural Michigan.

ple ^{12}C is characterized by both the elastic peak labelled in fig. 5 and the first inelastic group just below channel number 100. Similarly ^{14}N is characterized by the labelled elastic peak and that due to the proton group to the second excited state which occurs just above channel number 200. Although the majority of light elements have spectra which are simply described, the most complex case is depicted in fig. 6. The ^{27}Al spectrum requires about 15 Gaussian peaks for its description. This is similar to the situation with the L and M X-ray lines of Pb which need 17 Gaussian peaks for their description in our PIXE analysis program. It should be noted that in cases such as aerosol analysis only the dominant elastic ^{27}Al peak will be significant.

4. Applications

The PESA system was designed primarily for analysis of air particulate samples. An example of this application is shown as fig. 7 which is the scattering spectrum obtained by bombarding a Nuclepore filter particulate sample of relatively clean winter air from a rural area of southern Michigan.

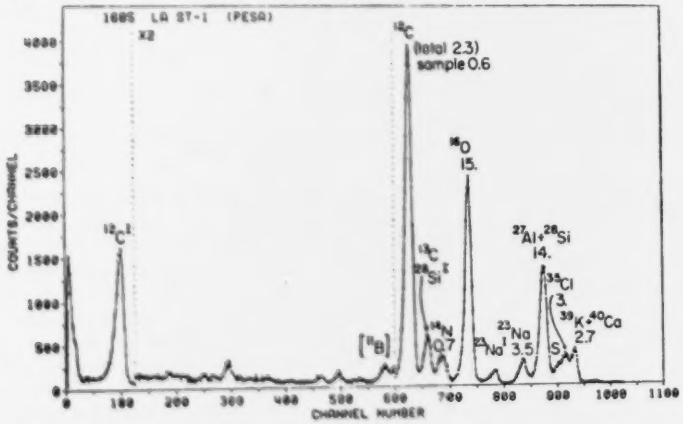

Fig. 8. PESA spectrum of a size fraction of particulate matter from a site near Los Angeles, Ca. The numbers above the peaks are the mass of that element in micrograms per cubic meter of air.

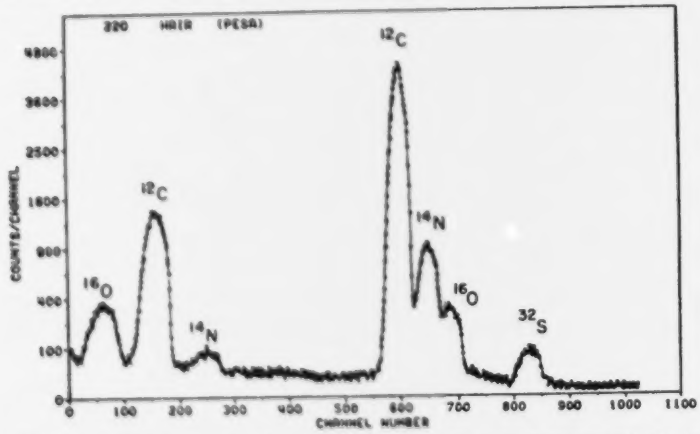

Fig. 9. PESA spectrum resulting from the bombardment of 2 mm of the root end of a human hair.

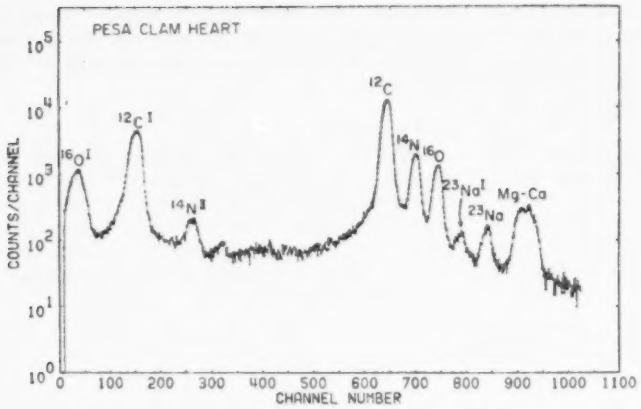

Fig. 10. Clam heart spectrum. Sample prepared by flattening between glass plates and freeze drying.

In this spectrum the ^{12}C and ^{16}O peaks are dominated by those isotopes contained in the filter itself. By contrast the spectrum[4]) shown in fig. 8 was taken by bombarding a thin polystyrene backed (100 $\mu g/cm^2$) sample in which case subtraction for the ^{12}C in the backing is feasible. The numbers above the peaks are the mass of that element in micrograms per cubic meter of air.

Although suitably thin biological samples are usually difficult to prepare, results have been achieved in several cases. Fig. 9 is the spectrum resulting from the bombardment of 2 mm of the root end of a single human hair. The somewhat broad peak labelled ^{32}S contains lesser amounts of P and Cl which were detected by PIXE analysis. For hair specimens of thicker cross section the resolution of adjacent peaks is not as complete as for those in fig. 9 but indications are that they can be evaluated with the aid of a computer code. Another example of a biological sample analysis is the clam heart spectrum shown as fig. 10. Clam hearts are normally too thick to permit resolution of adjacent peaks. This difficulty was overcome by flattening the heart between two glass plates.

5. Conclusions

A quantitative elemental analysis system utilizing proton elastic scattering analysis for light element determinations has been developed. For thin samples (1 mg/cm^2 or less) the method is absolute, multi-element, rapid (minutes) and non-destructive of the prepared sample. In conjunction with proton induced X-ray emission analysis, it forms a system capable of measurement of all elements within its detection limits. Extensive application to the analysis of atmosphere particulate matter have begun and feasibility studies for biological samples are being explored.

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